

Rietveld Refinement as a Structural Tool

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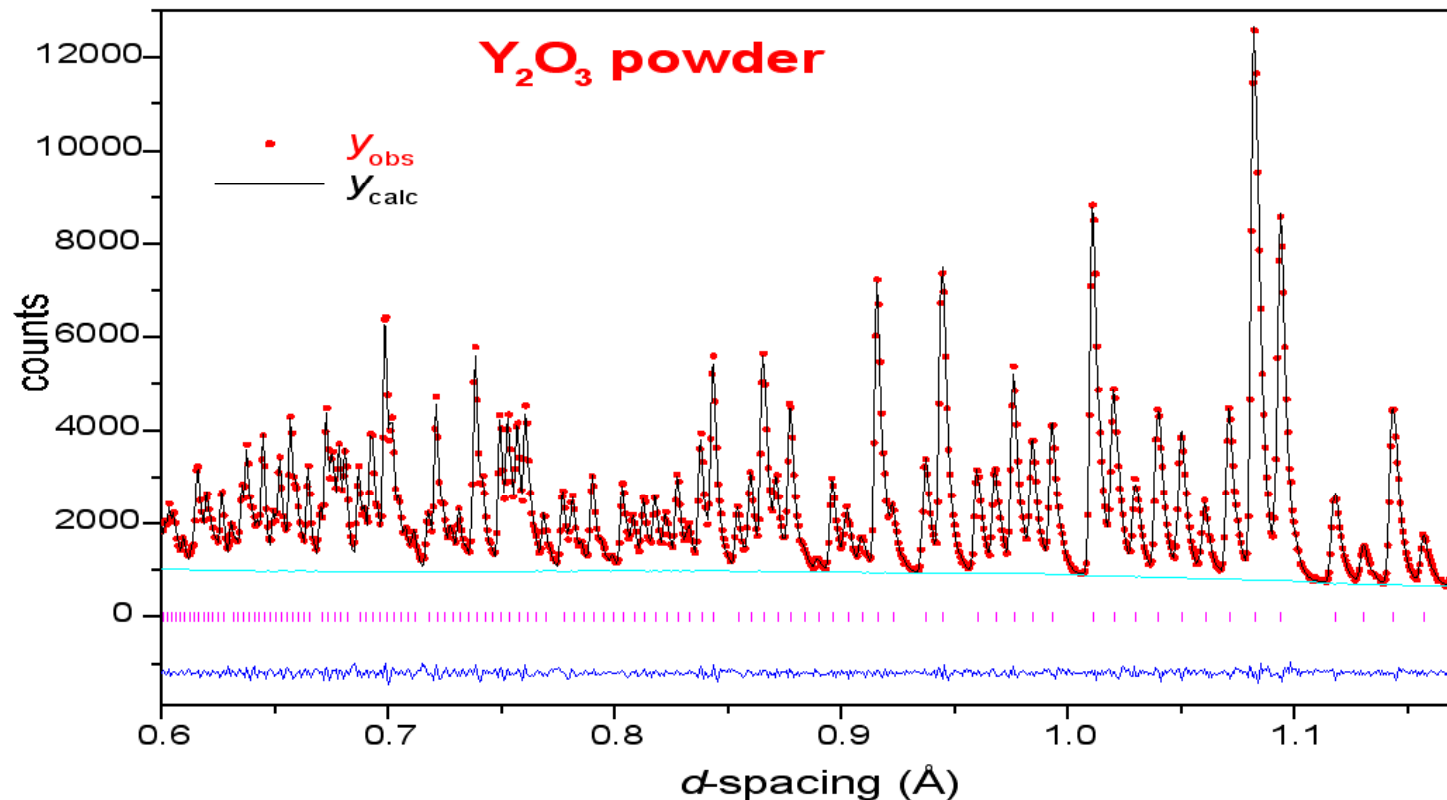
Preview of the Talk

- Outline the basic principles of Rietveld refinement
- Give examples of how Rietveld refinement has been used to address important problems in chemistry, materials science, and solid state physics
- Offer some advice on how to obtain meaningful results while avoiding common pitfalls

Disclaimer

- The talk is intended to be illustrative, not comprehensive.
- My choices of examples are what I'm most familiar with, not necessarily the most important work.
- My use of Rietveld refinement is usually to investigate structure-property relationships, not to determine structures.

How is structural information manifest in a powder diffraction pattern?



1. Unit cell dimensions determine peak positions
2. Atom positions and thermal vibrations determine peak intensities

Diffraction profile of Y_2O_3 contains 198 independent Bragg peaks ($0.5 \leq d \leq 4.0 \text{ \AA}$). How many parameters determine all the peak positions and intensities?

1. Unit cell dimensions determine peak positions

$$d_{hkl}^{-2} = h^2 a^{*2} + k^2 b^{*2} + l^2 c^{*2} + 2hka^*b^*\cos\gamma^* + 2hla^*c^*\cos\beta^* + 2klb^*c^*\cos\alpha^*$$

A maximum of 6 parameters: $a, b, c, \alpha, \beta, \gamma$

2. Atom positions and thermal vibrations determine peak intensities

$$F_{hkl} = \sum_j N_j b_j \exp\left[\frac{B_j}{4d_{hkl}^2}\right] \exp\left[2\pi i(hx_j + ky_j + lz_j)\right]$$

Where:

N_j	site occupancy of j th atom
b_j	scattering length of j th atom
B_j	isotropic temp. factor of j th atom
x_j, y_j, z_j	position of j th atom within unit cell

Y_2O_3 structure parameters:
 unit cell: 1
 atom positions: 4
 iso. temp. factors: 3

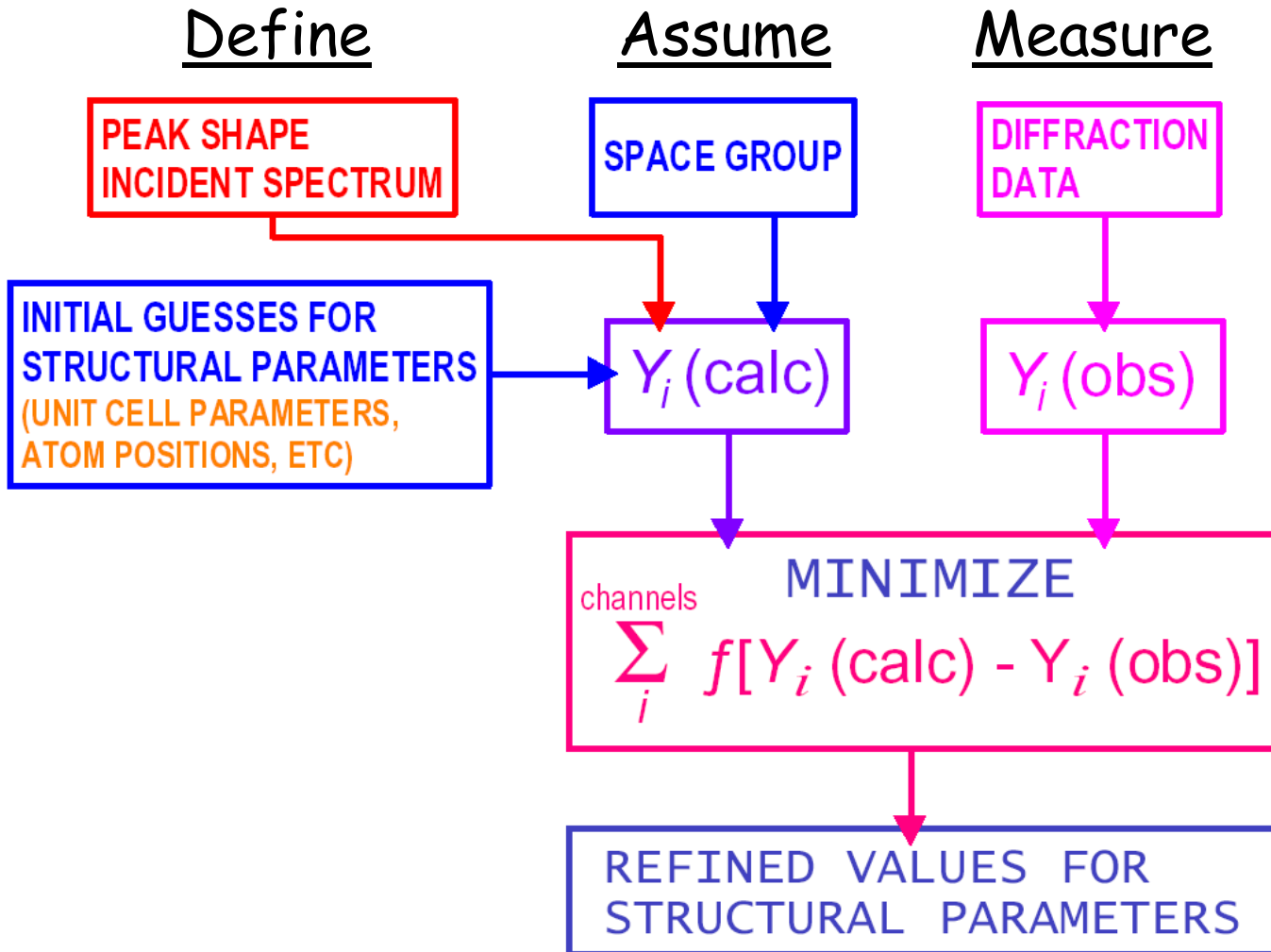
Rietveld Refinement: Simple Definition

- Rietveld structure refinement is a method for estimating the intensities of Bragg peaks in a powder diffraction pattern within the constraints imposed by a particular unit cell Symmetry and crystallographic space group.
- Moreover, there is no need to extract the individual Bragg intensities as an intermediate step. We can extract the physical variables of interest directly from the diffraction data by constrained least-squares minimization.

This first person to realize and demonstrate this was Hugo Rietveld.

[H. M. Rietveld, J. Appl. Cryst. 2, 65 (1969)]

Architecture of a Rietveld Refinement Code



Advantages of Powder Diffraction and Rietveld Refinement

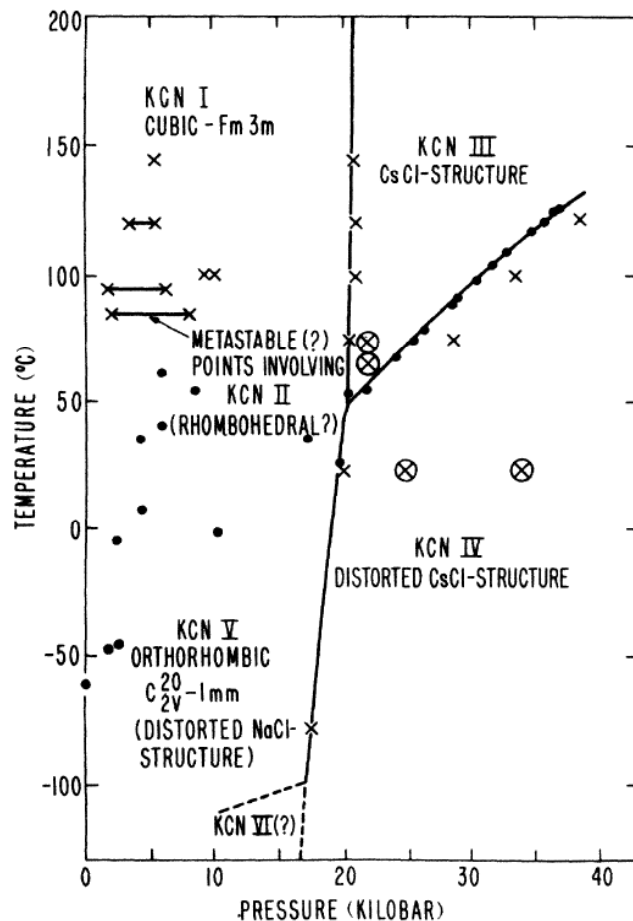
- Strict test of a proposed model
- Single crystals not available
- "Real" samples
- Mixed phases
- Quantitative analysis
- Structural changes vs. temperature, pressure, etc.
- Systematic modifications of a known "host" structure
- Defects in a known structure

Neutron diffraction study of KCN III and KCN IV at high pressure*

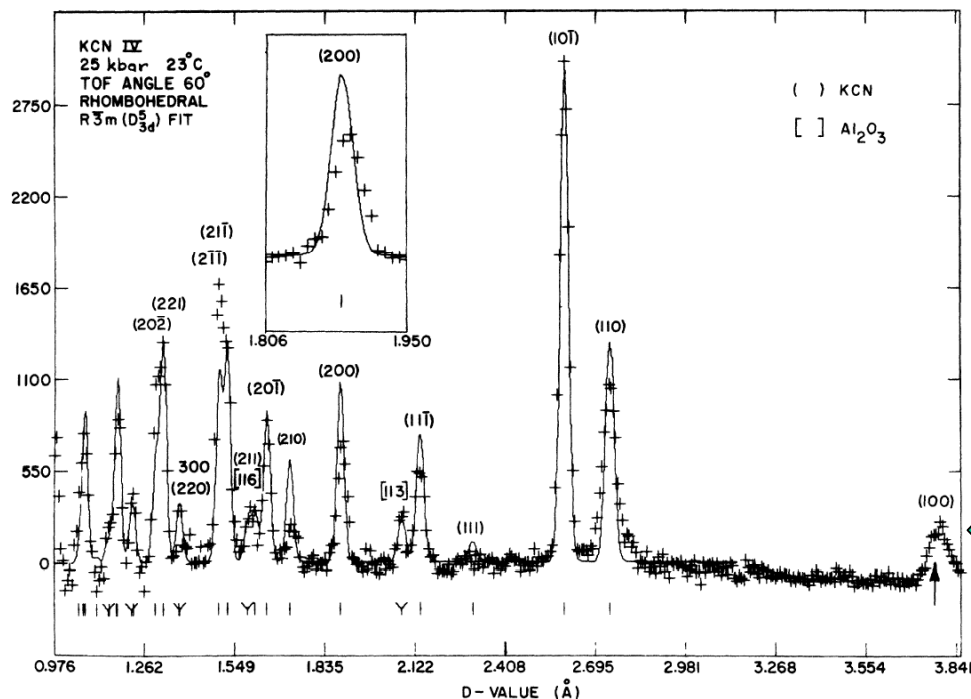
D. L. Decker,[†] R. A. Beyerlein, G. Roullet,[‡] and T. G. Worlton

Argonne National Laboratory, Argonne, Illinois 60439

(Received 27 September 1973)

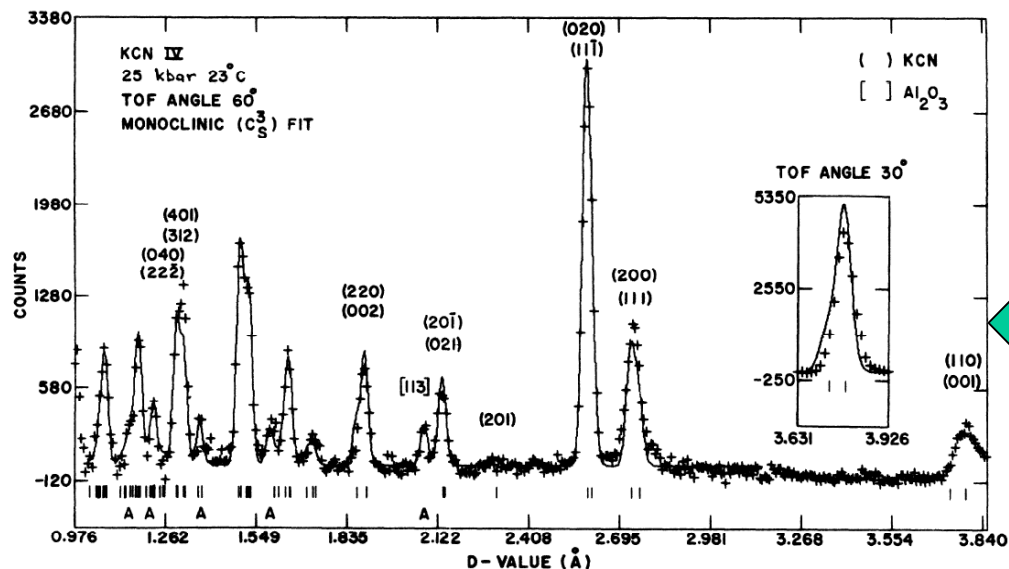


The First Rietveld Refinement in the United States?



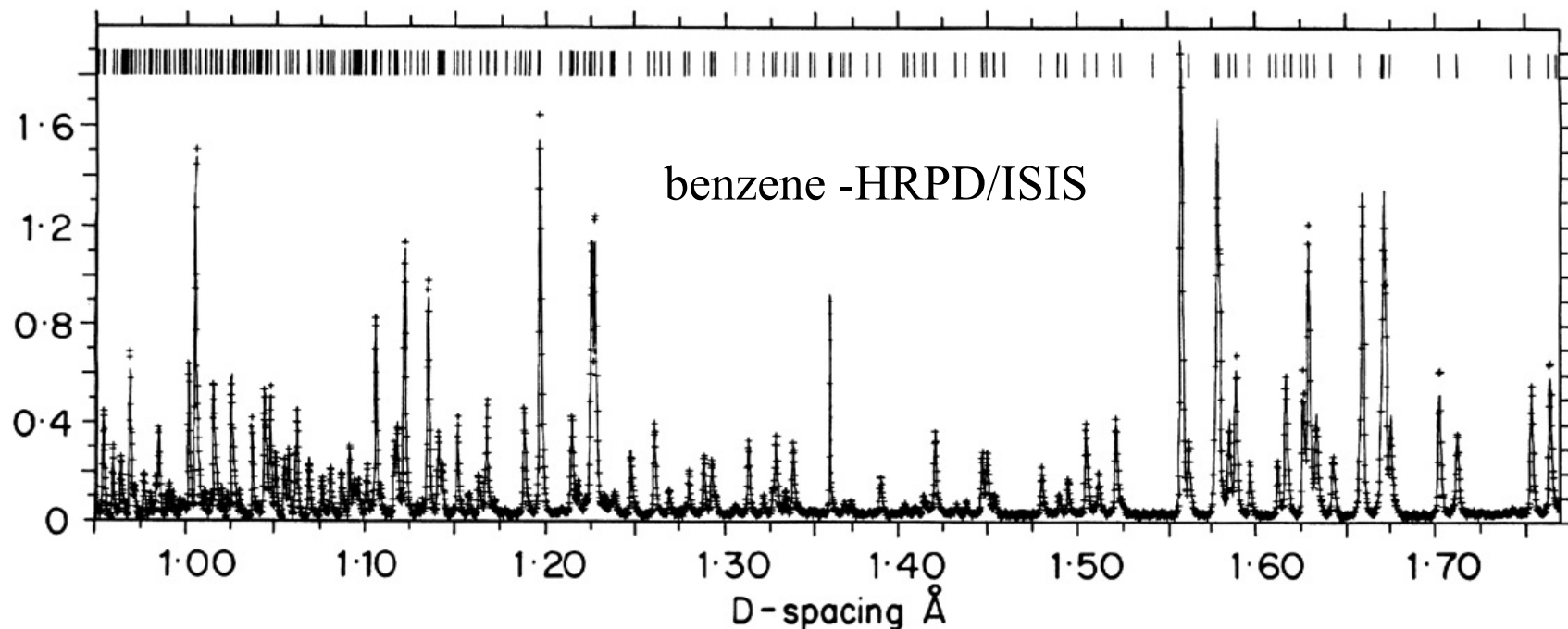
The Structure of KCN IV

Incorrect
R3m model



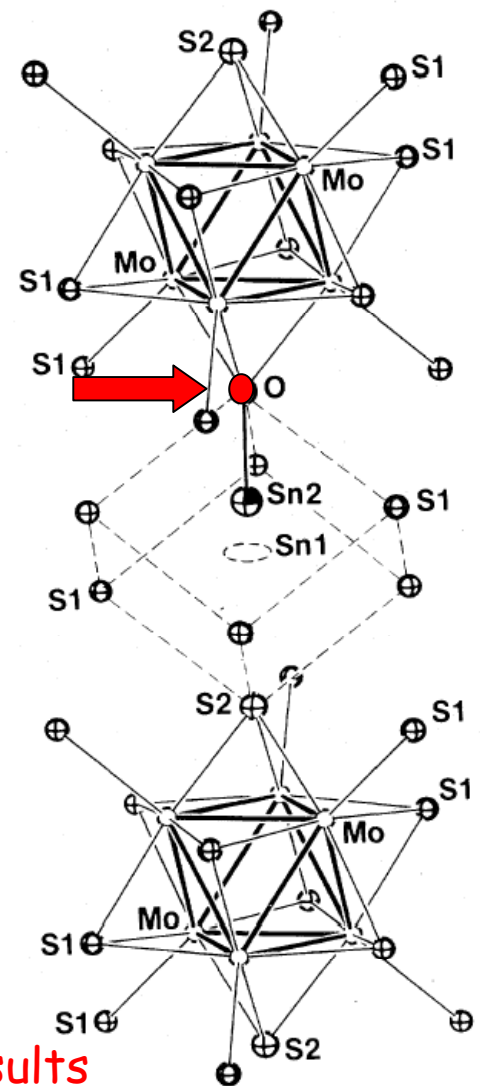
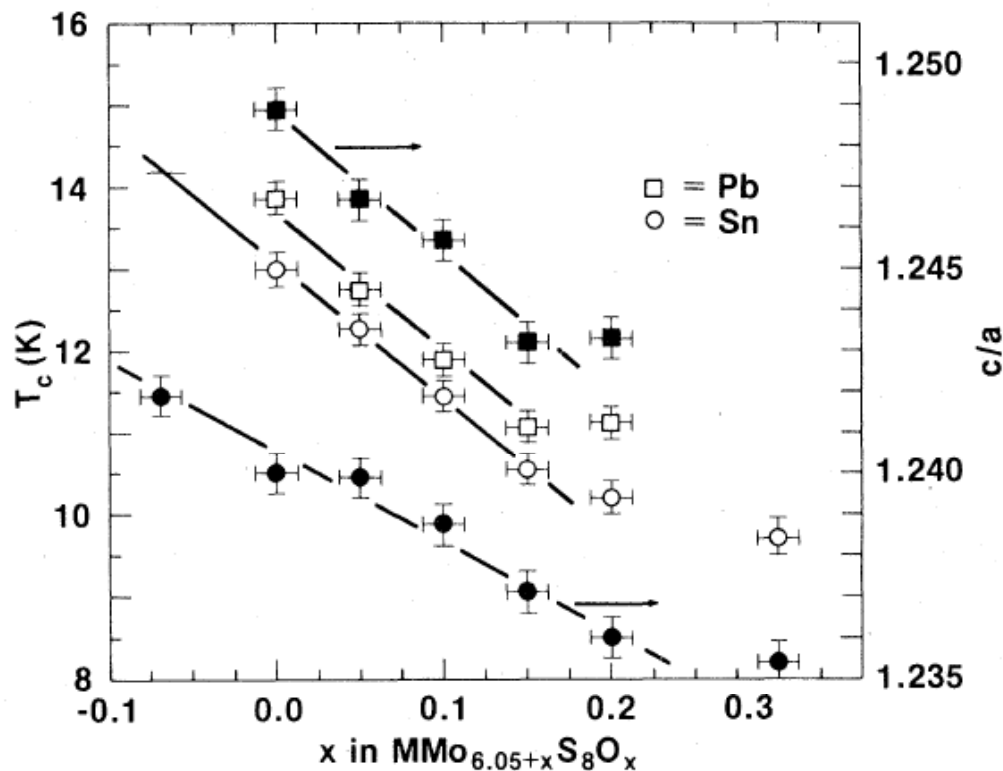
Correct
Cm model

If important results can be obtained from such crude data, imagine what can be learned from data like these:



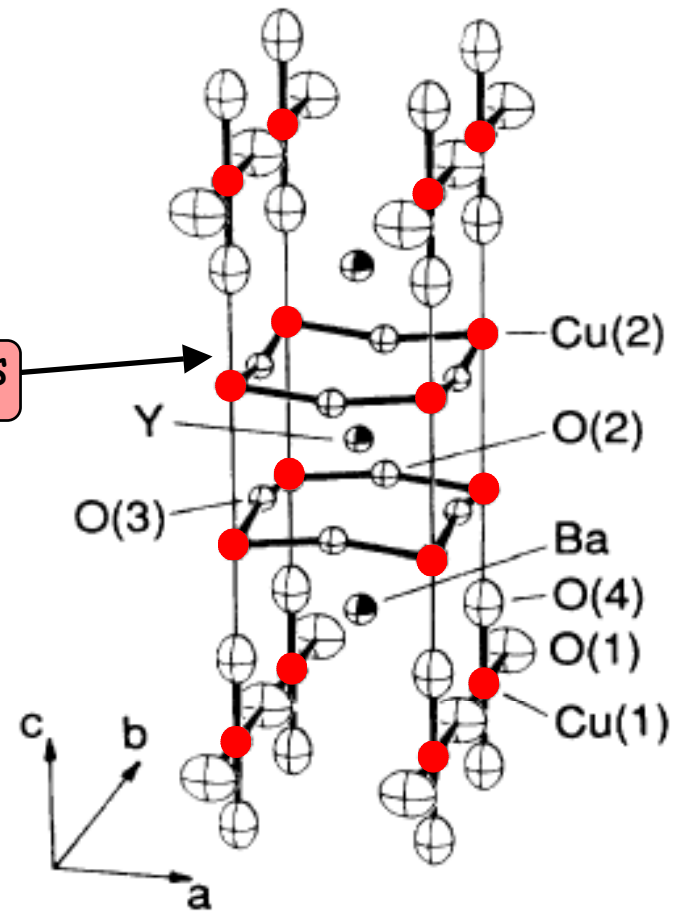
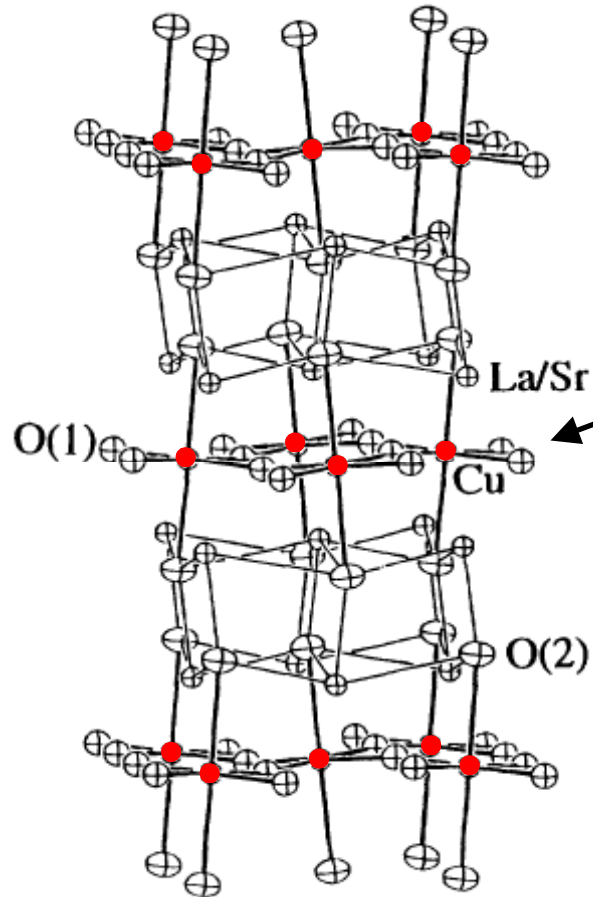
W. I. F. David and J. D. Jorgensen, in The Rietveld Method, edited by R. A. Young, (International Union of Crystallography, Oxford Univ. Press, 1993) pp. 197-226

The Oxygen Defect that Lowers T_c in $\text{Sn/PbMo}_6\text{S}_8$

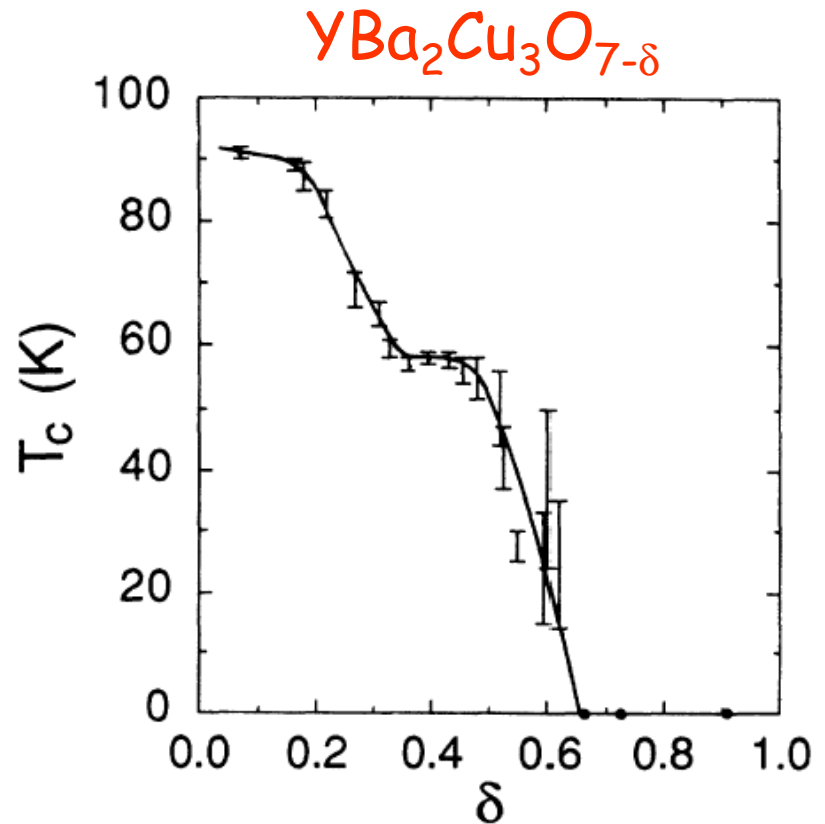
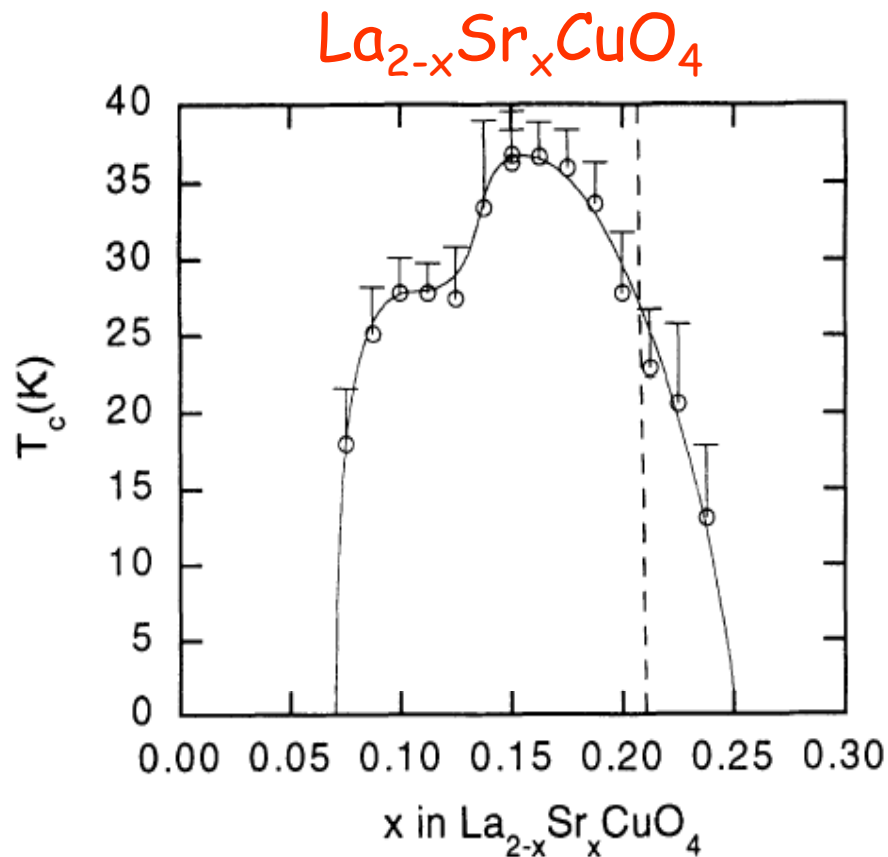


Example of the importance of correlating Rietveld results with other data to confirm the validity of the model.

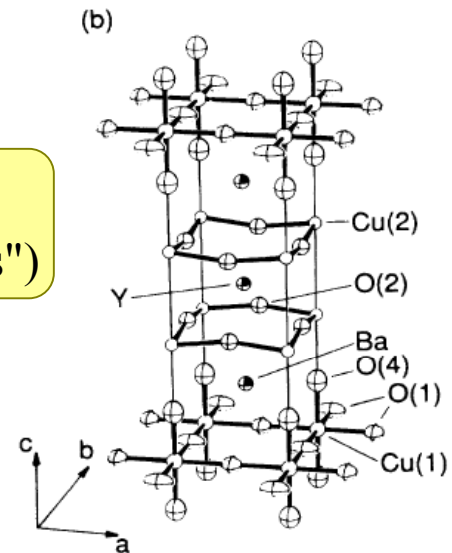
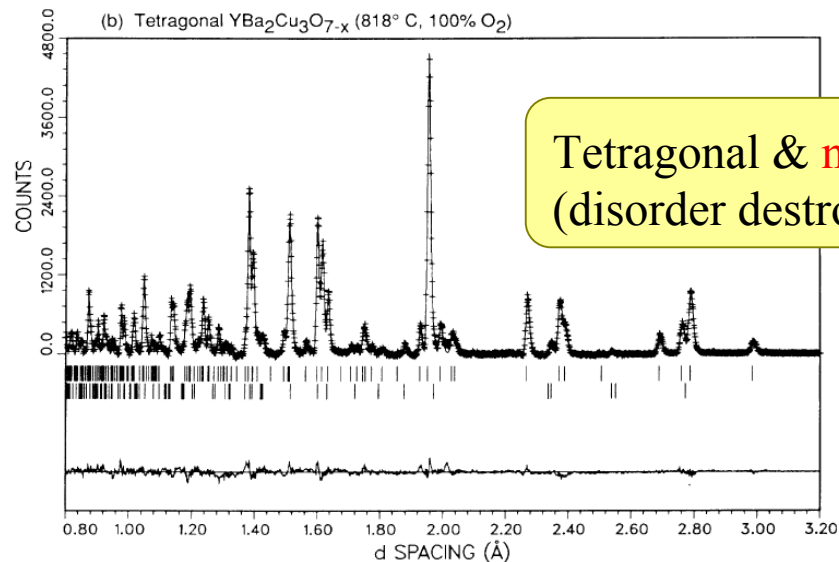
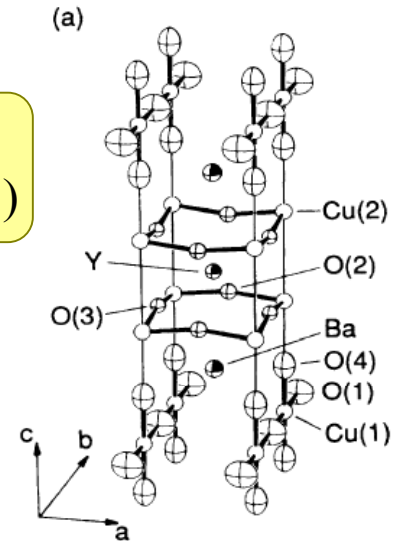
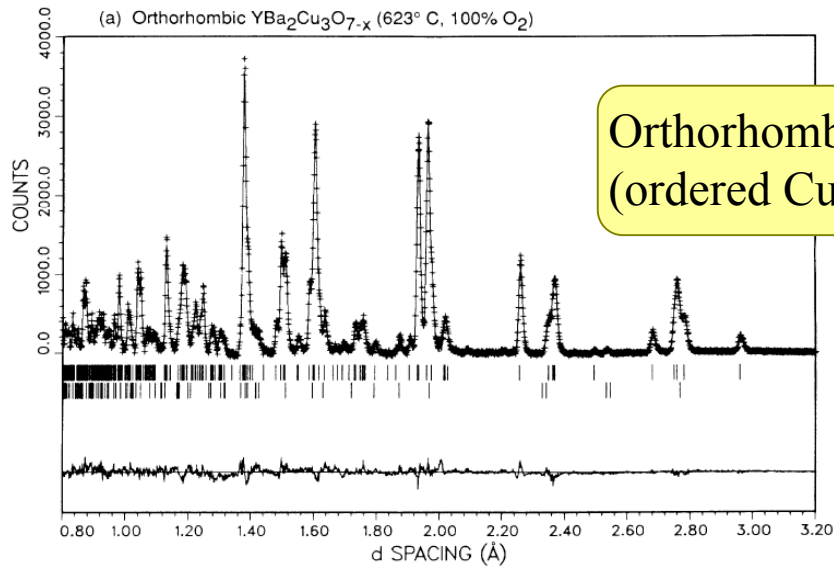
HTS Structures



How does composition/structure control the T_c ?

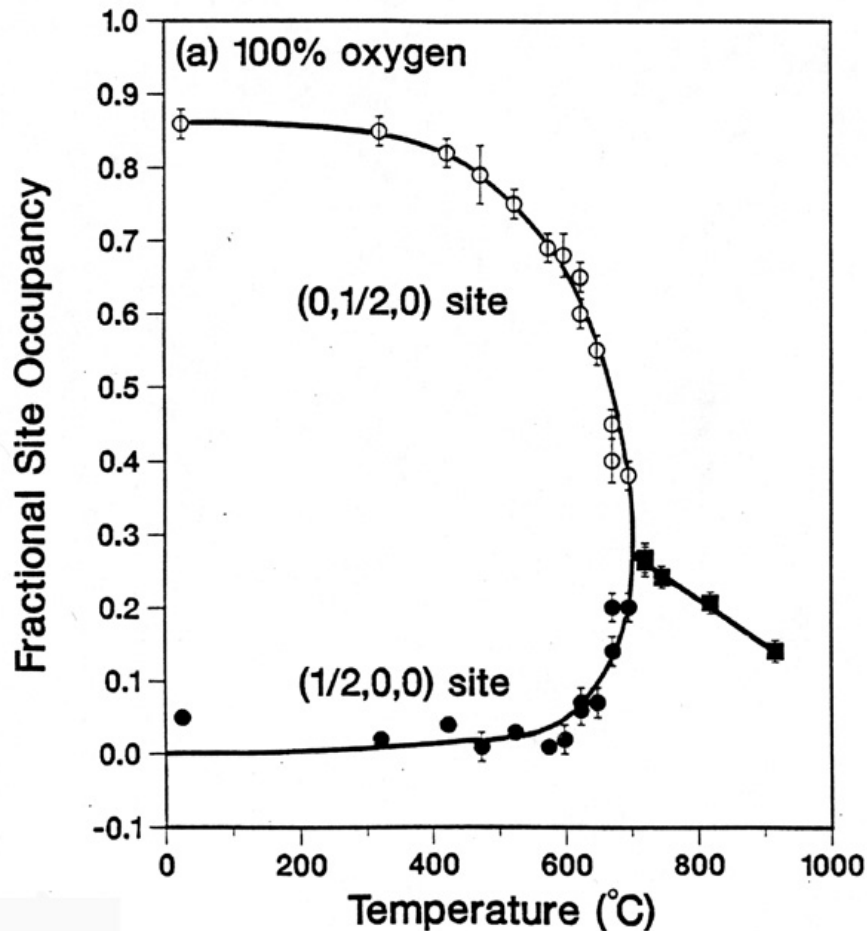


Two Structures for $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$



Controlling T_c Through Synthesis:

The degree of chain order can be varied continuously.

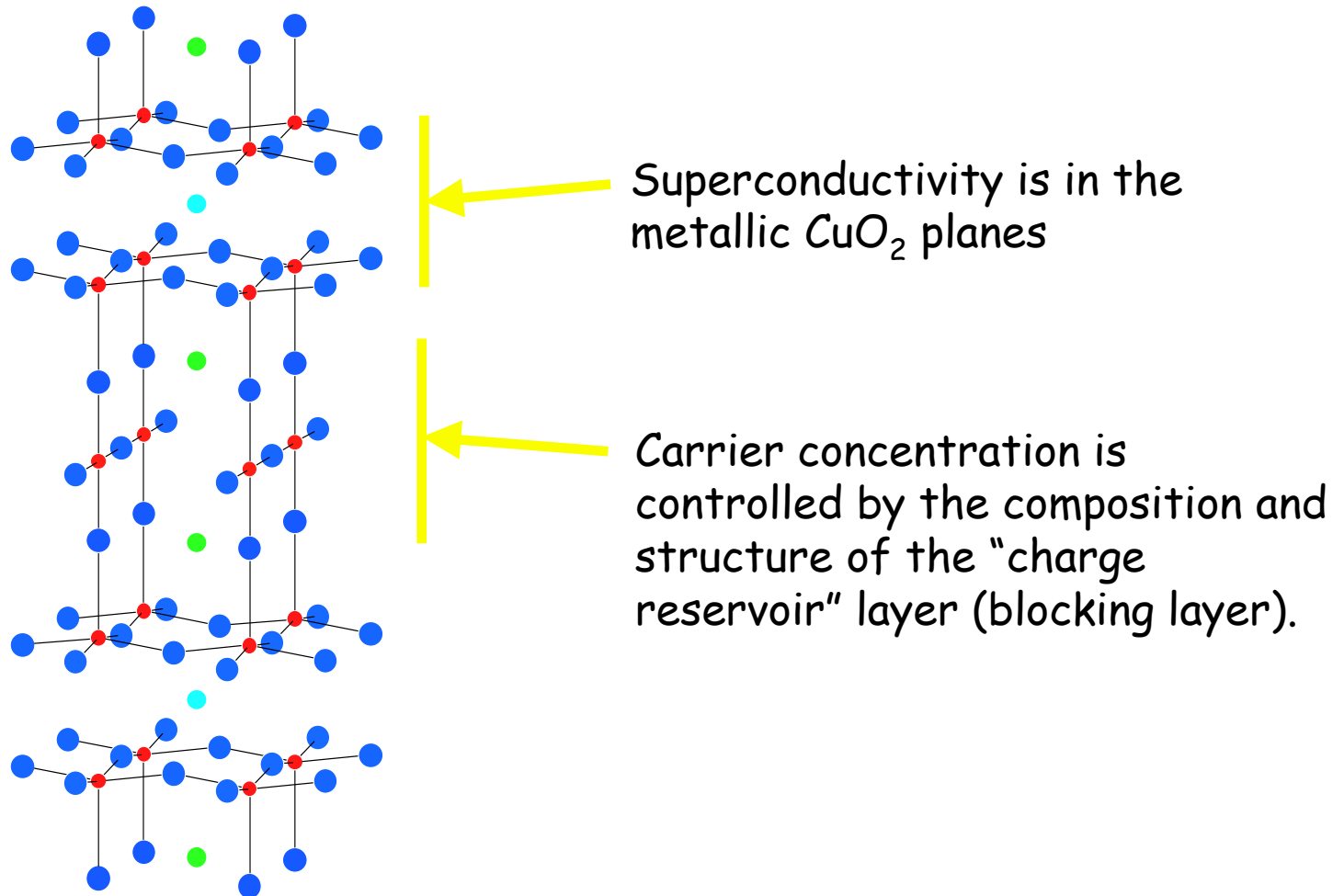


Oxygen content and ordering in $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ as a function of temperature in 1 atm oxygen.

Determined by in situ neutron powder diffraction

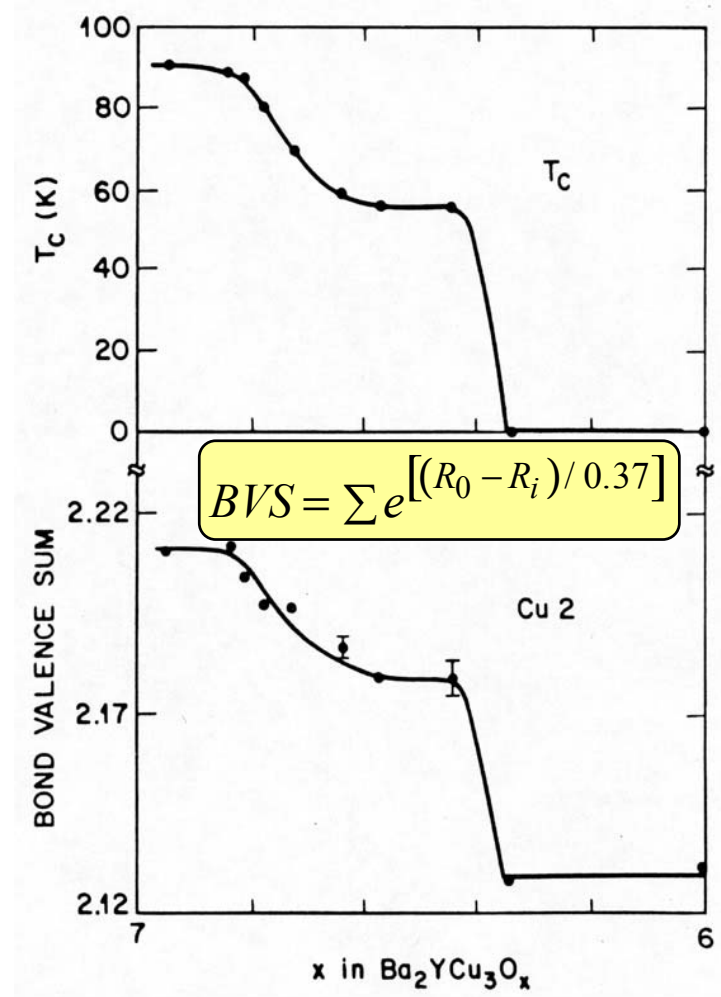
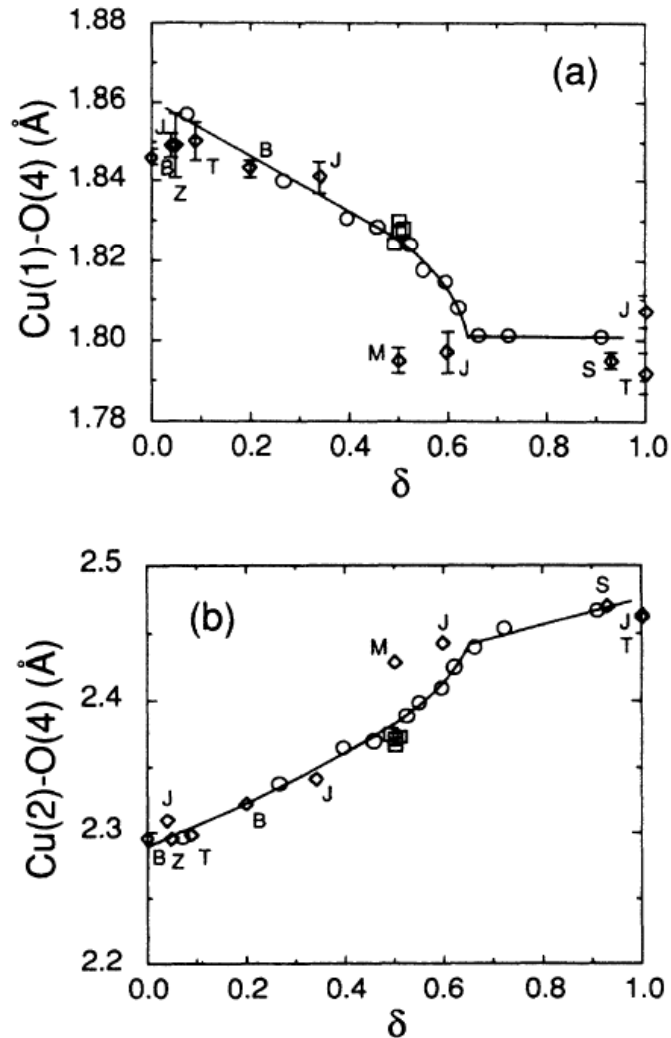
Jorgensen et al., Phys. Rev. B 36, 3608 (1987)

Charge Transfer Model for HTS



Evidence for the Charge Transfer Model

$\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$

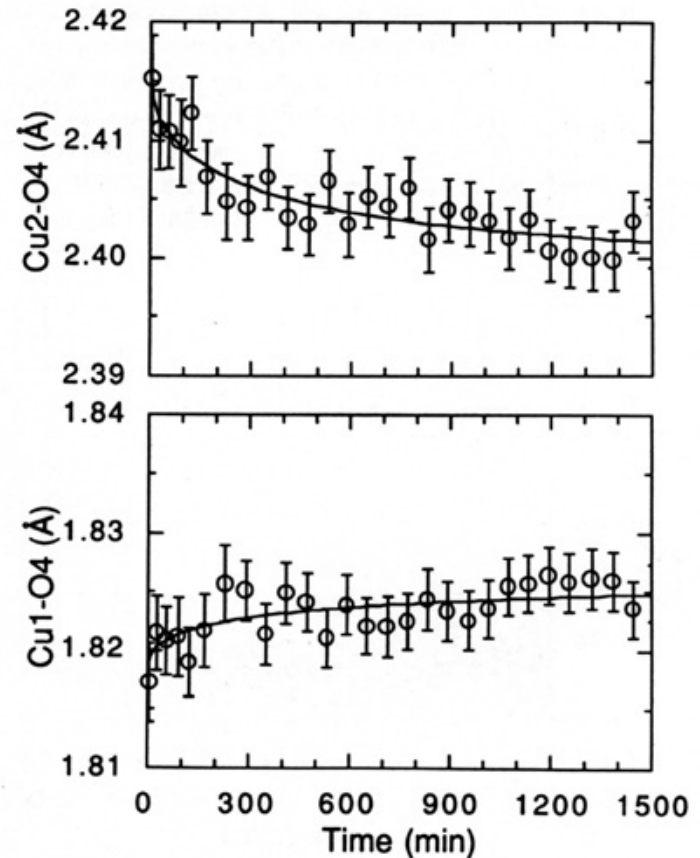
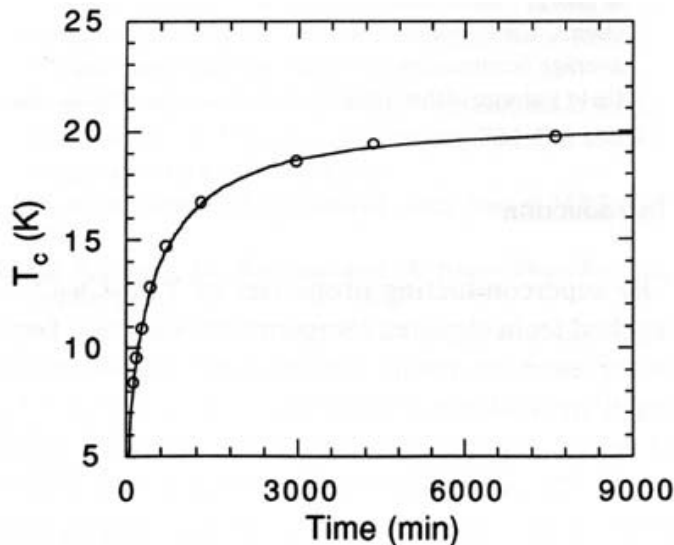


Cava et al., Physica C 165, 419 (1990)

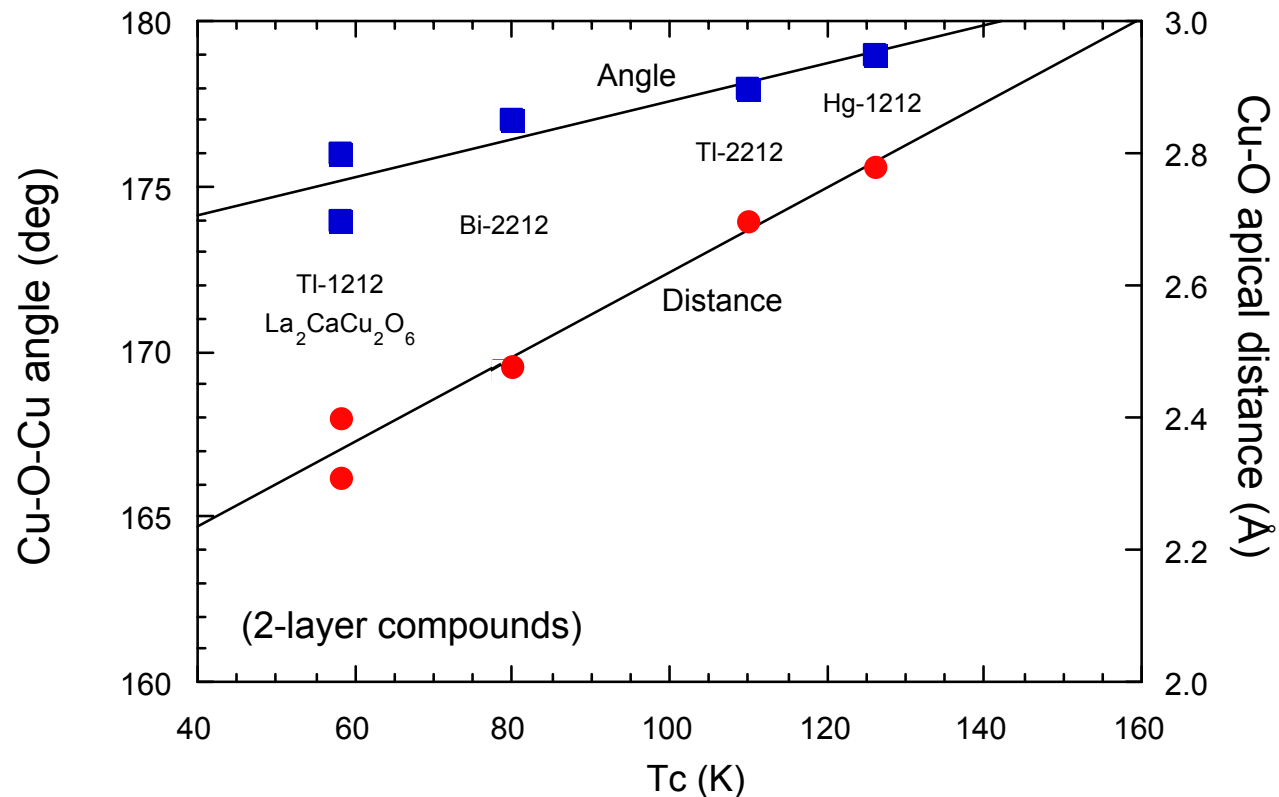
And... There were some surprises.

Time-dependent changes in T_c of Y-123 due to room-temperature oxygen diffusion.

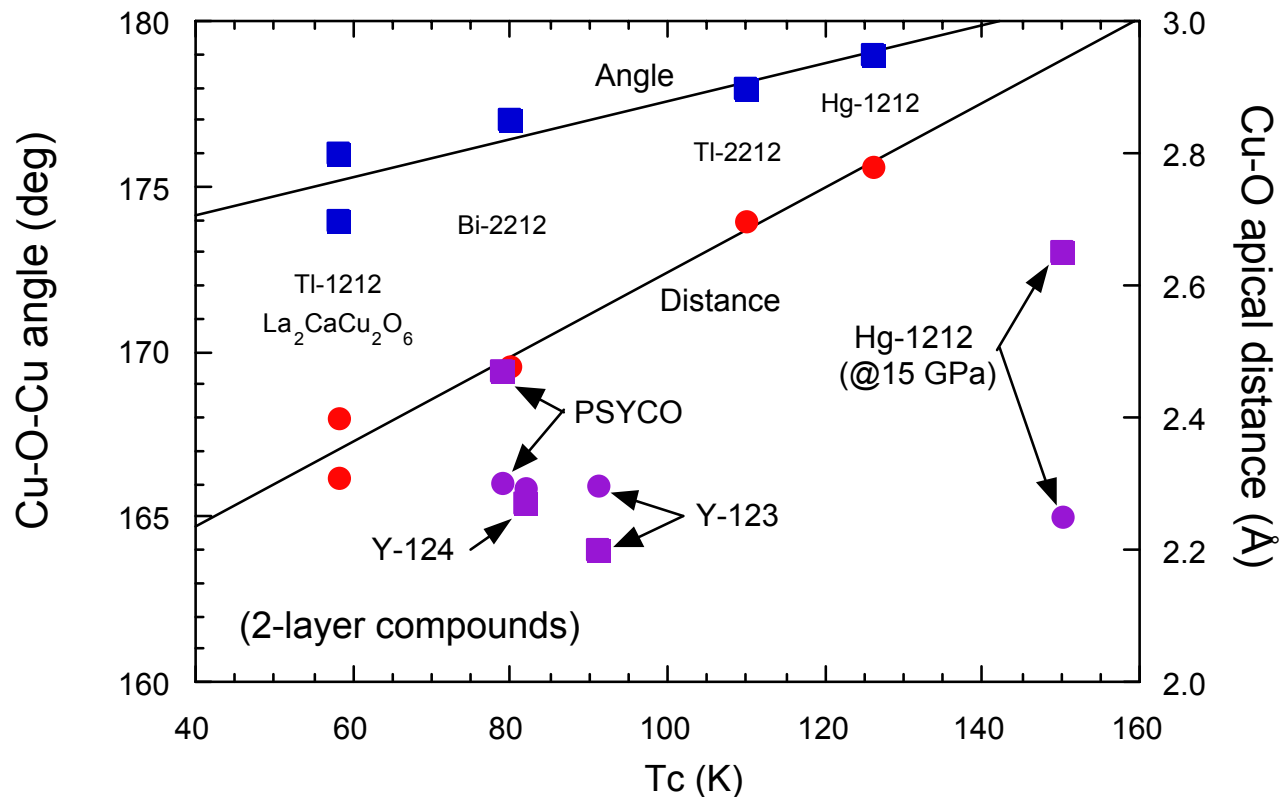
For samples quenched from high-Temp., T_c changes with annealing time at room Temp. due to time-dependent charge transfer.



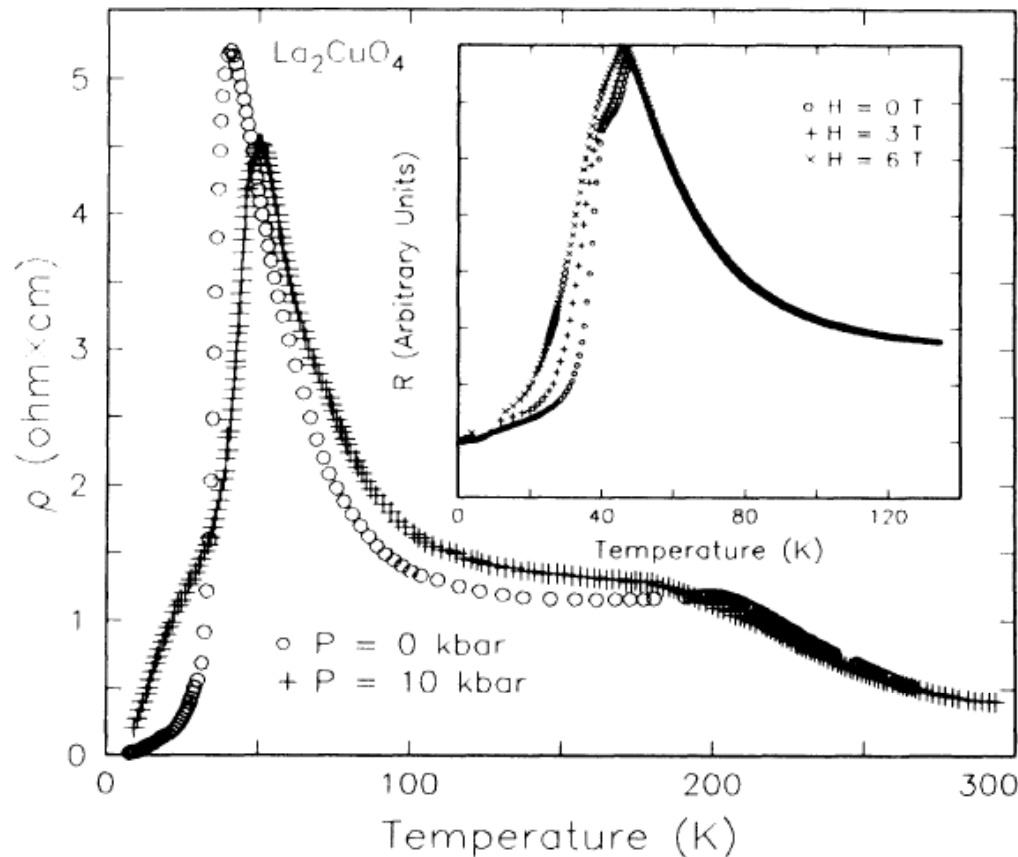
The Optimum Structure for High T_c : Flat CuO_2 planes



“Metallizing” the blocking layer is
another way to raise T_c

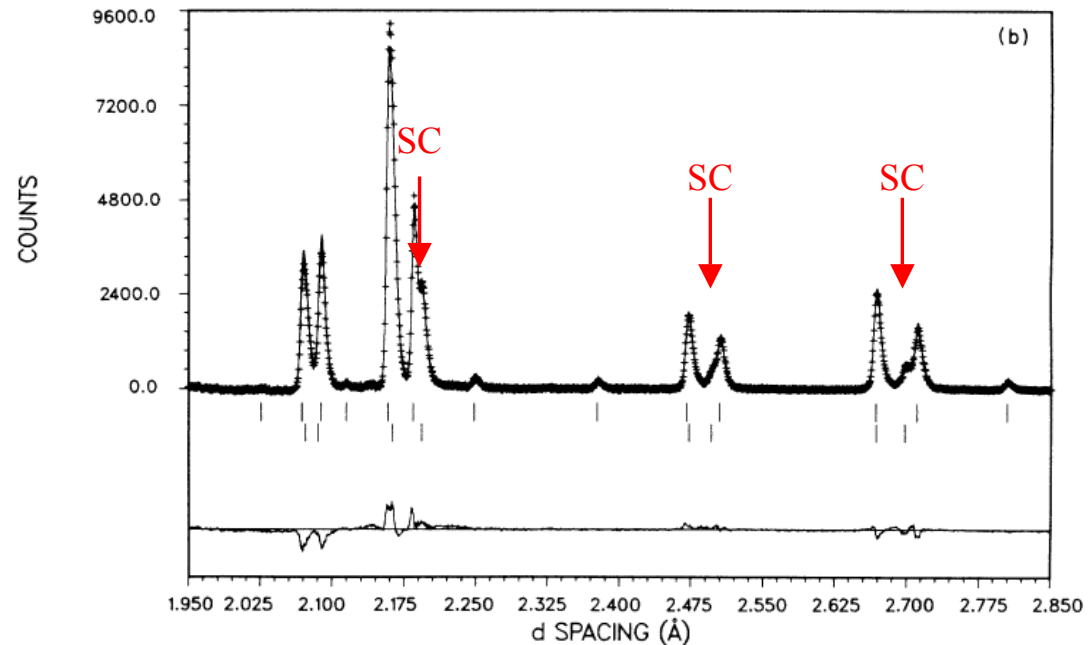
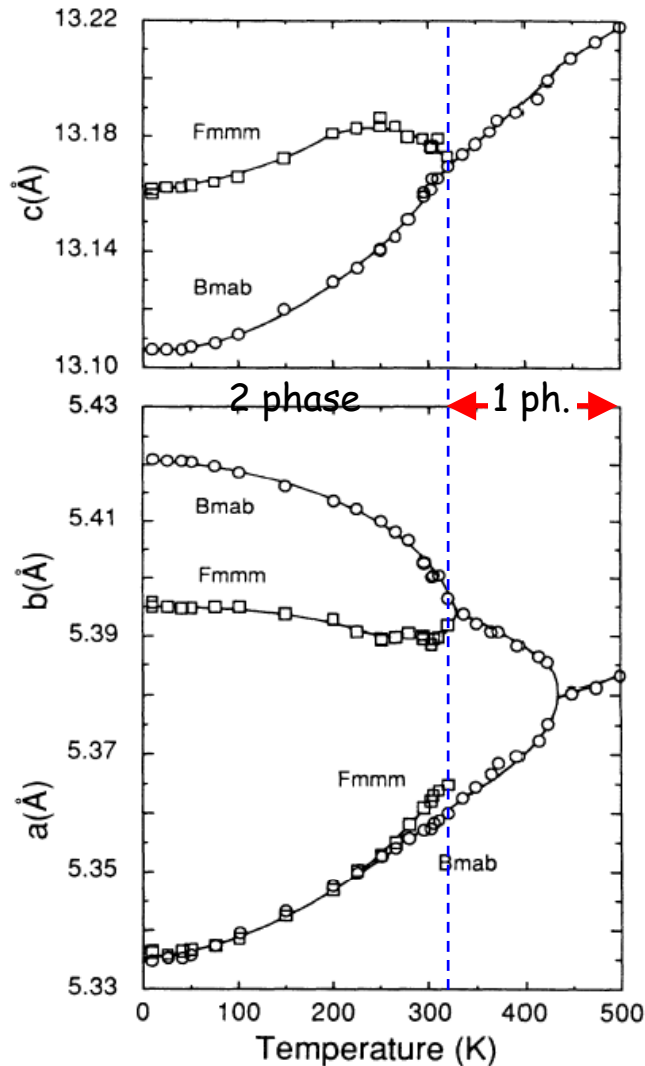


What about chemical inhomogeneity in HTS compounds?



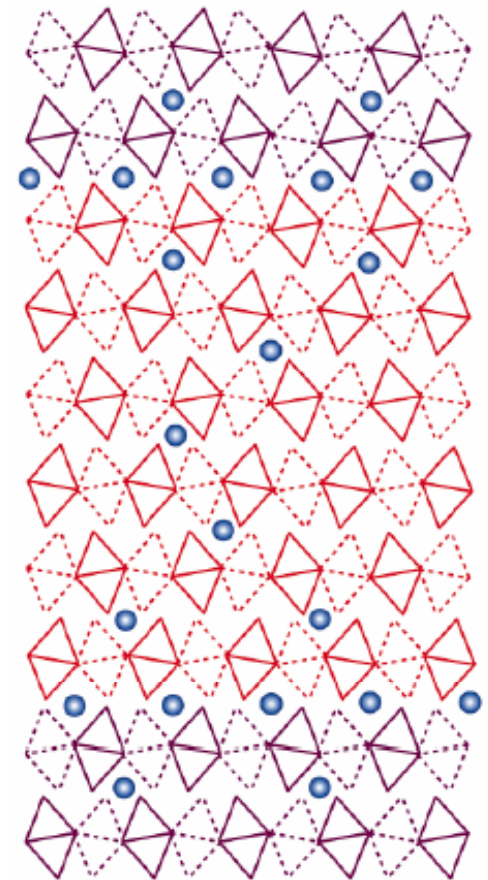
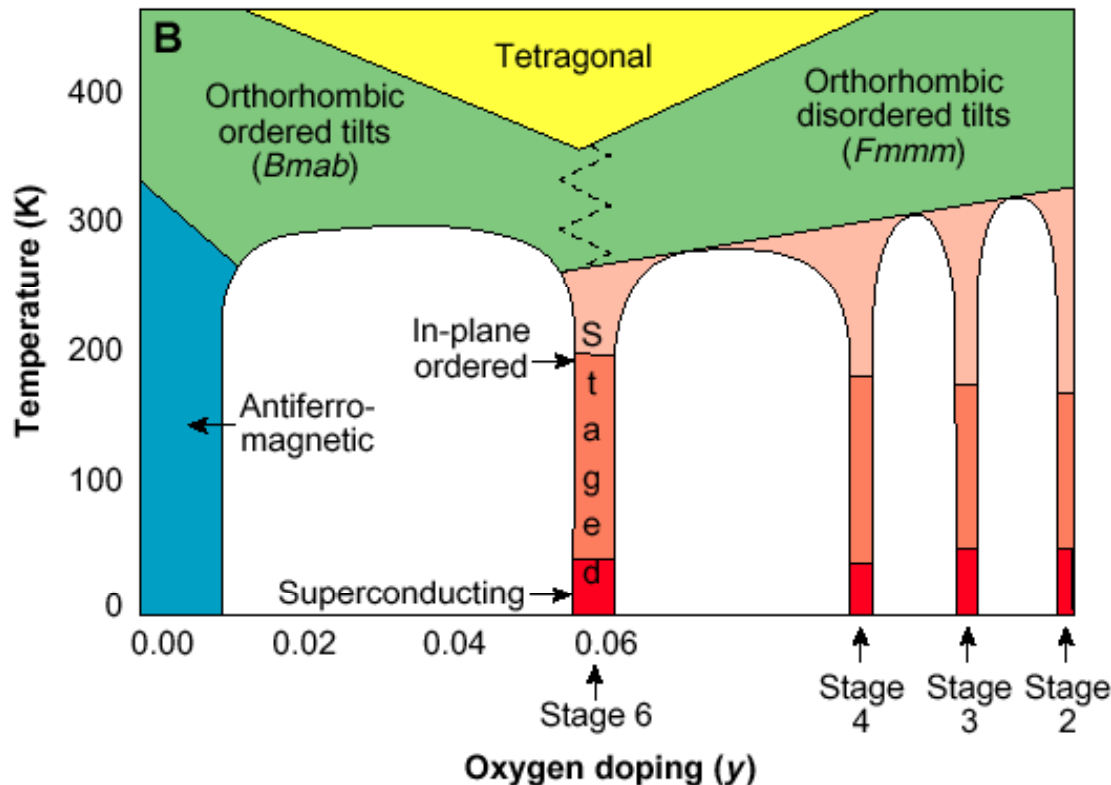
Data for La_2CuO_4 from some labs showed what appeared to be an insulator mixed with a superconductor. This was only seen in samples cooled slowly in oxygen (or high-pressure oxygen).

High-resolution neutron powder diffraction showed phase separation near room temperature into an oxygen-rich superconducting phase and a stoichiometric insulating phase.



Jorgensen et al., Phys. Rev. B 38, 11337 (1988)

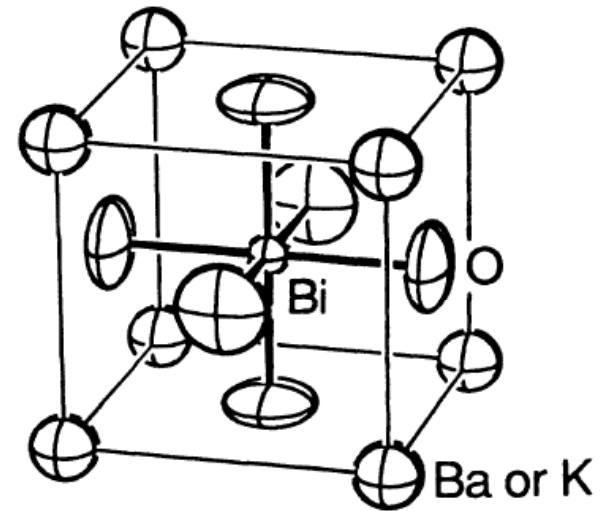
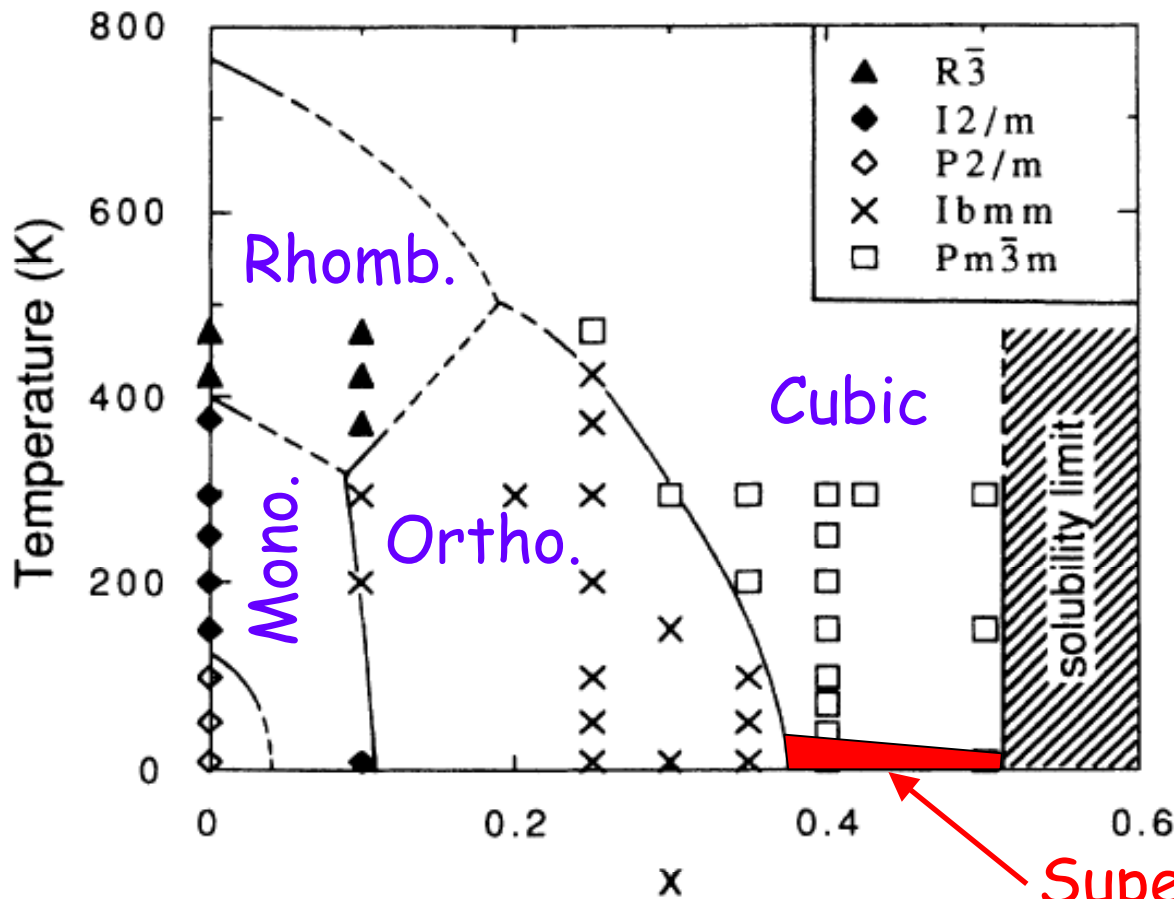
Ultimately, the phase separation was found to be much more complex than originally realized, with multiple miscibility gaps and staging of the interstitial oxygen defects.



Stage 6 structure

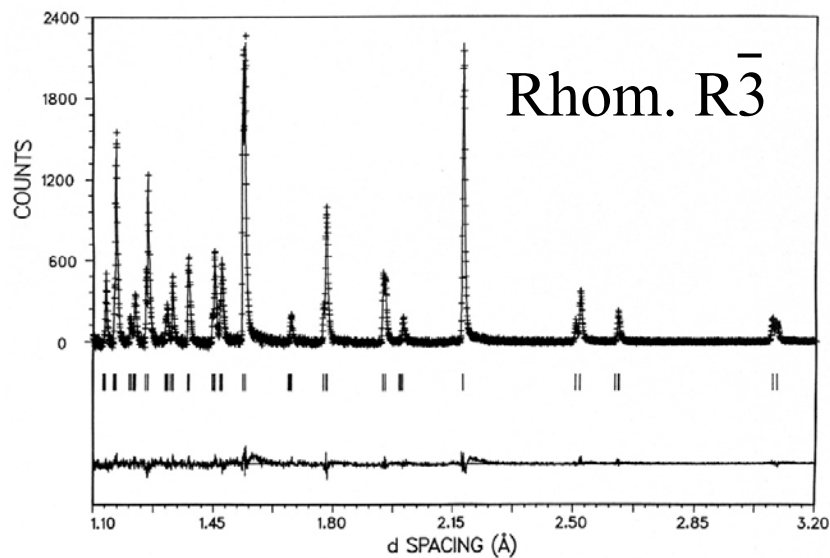
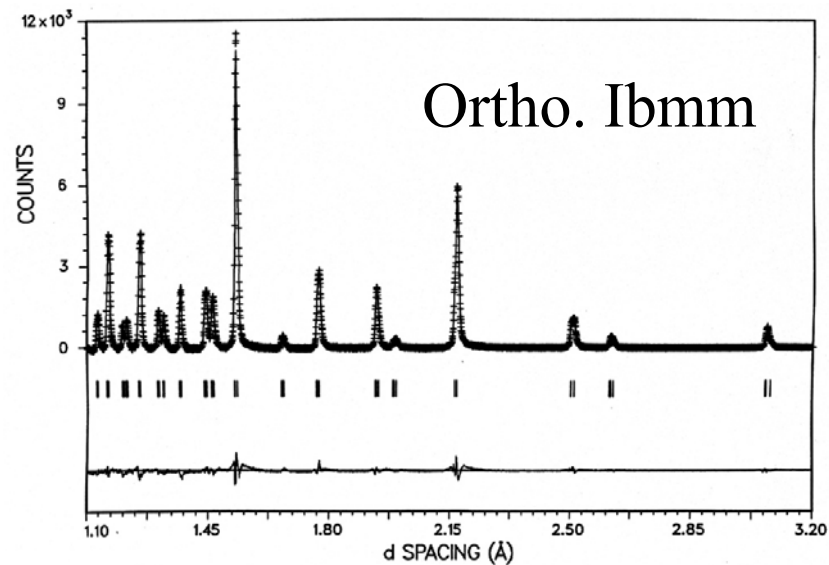
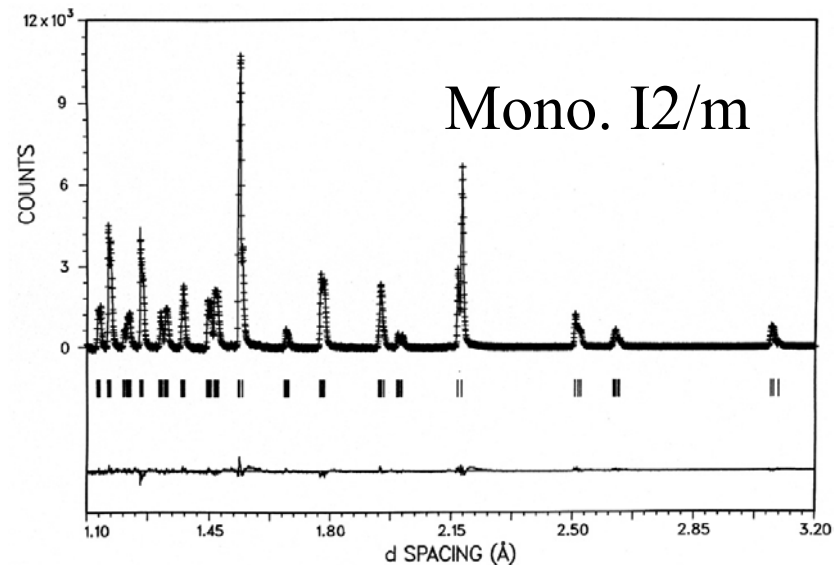
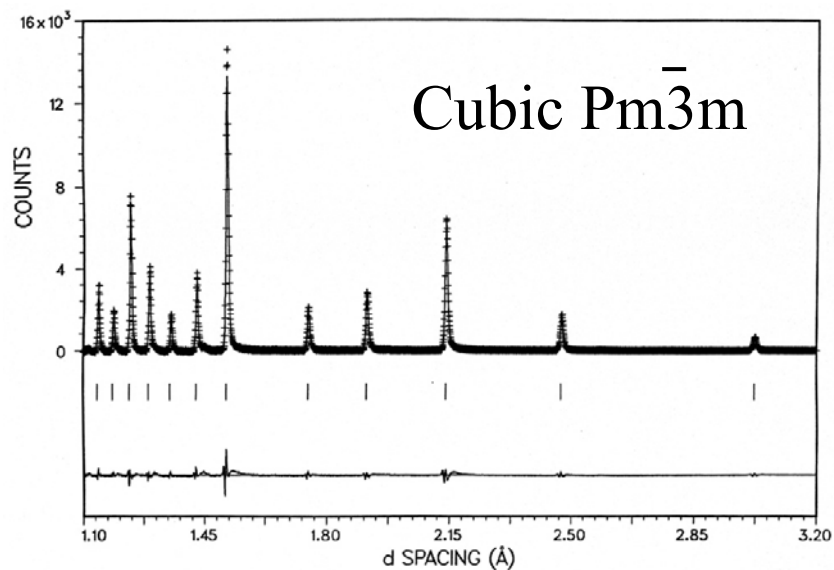
Wells et al., Science 277, 1067 (1997)

Superconductivity in $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ (only in the cubic phase)

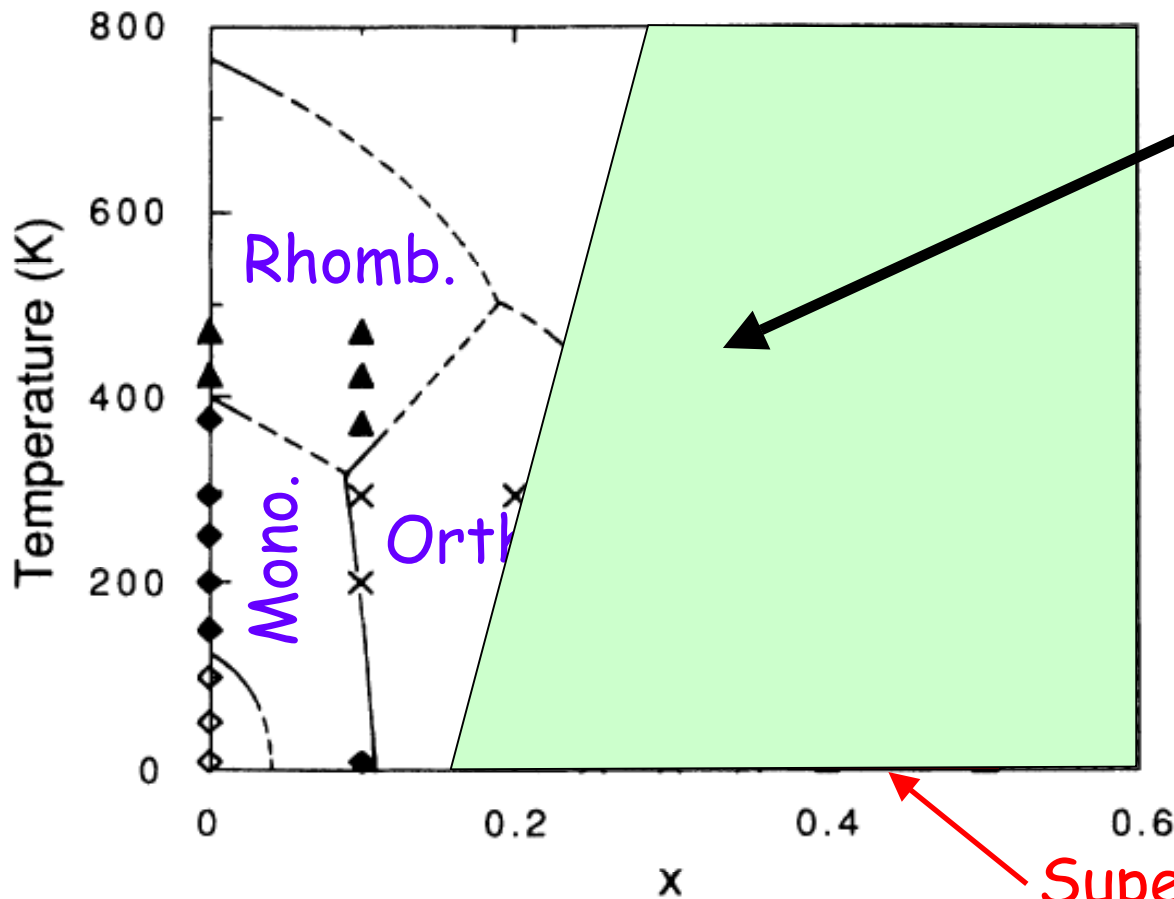


Superconductivity

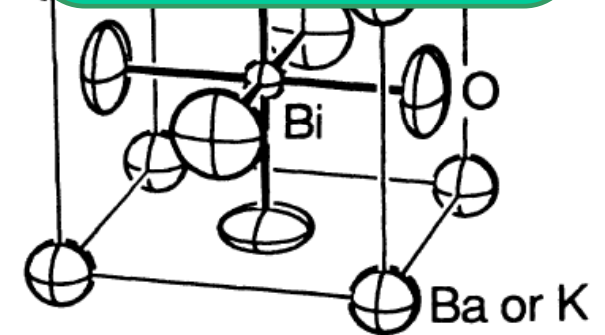
Rietveld Refinement Profiles for $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ Phases



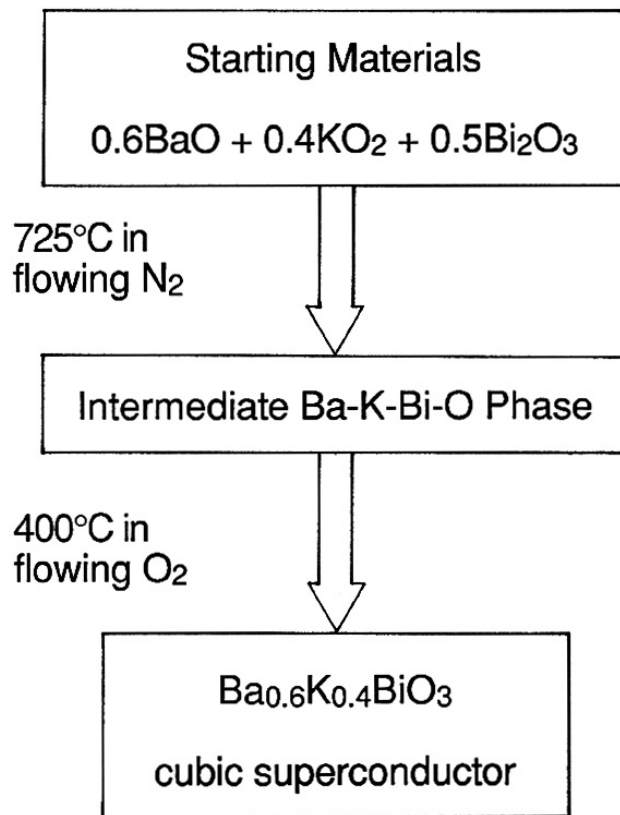
Superconductivity in $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ (only in the cubic phase)



But, these compositions are metastable!



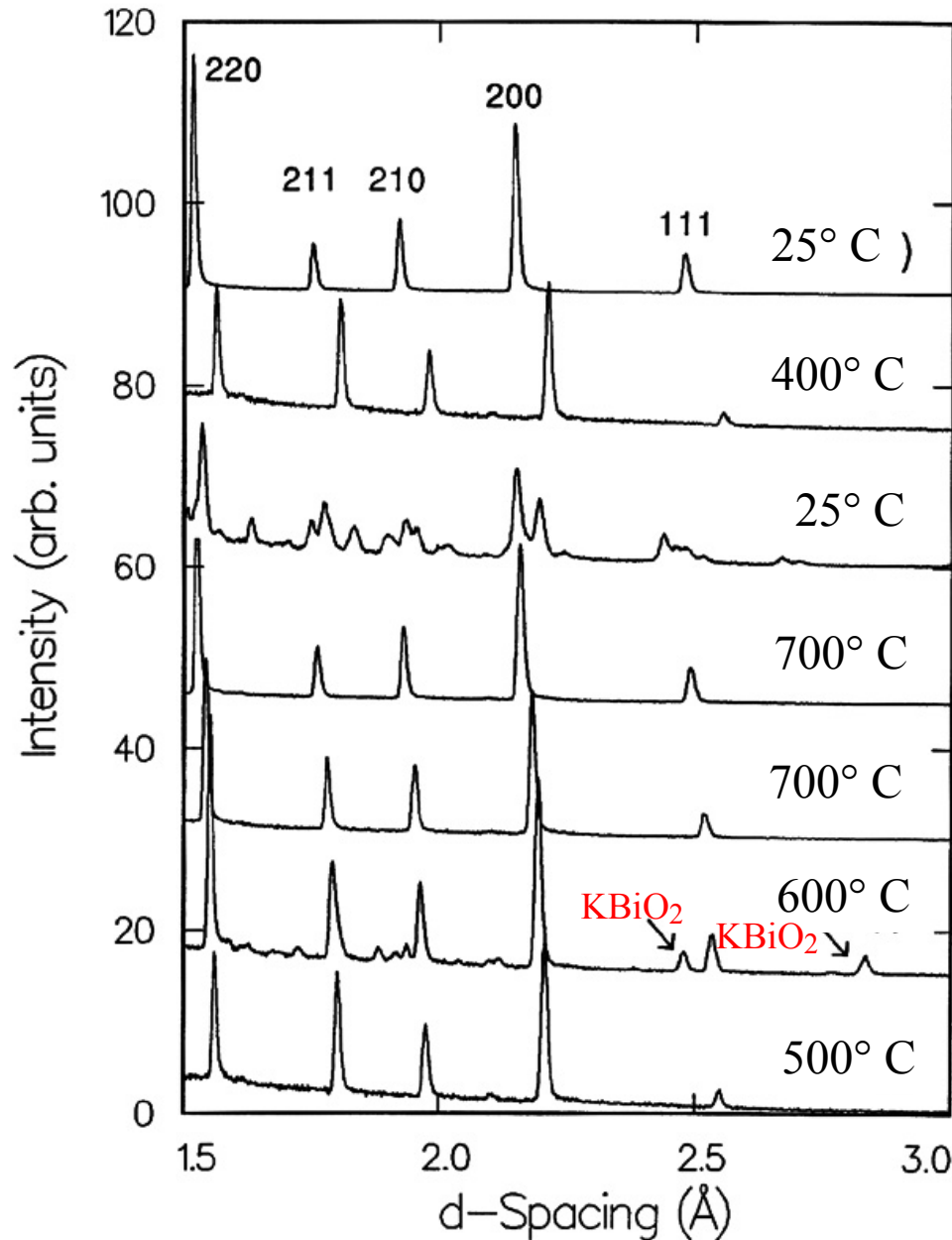
Because the superconducting composition of $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ is metastable, it must be made in a two-step process.



In situ neutron powder diffraction was used to understand this synthesis chemistry.

Pei et al., J. Solid State Chem. 95, 29 (1991)

Synthesis Chemistry of $\text{Ba}_{1-x}\text{K}_x\text{BiO}_{3-\delta}$



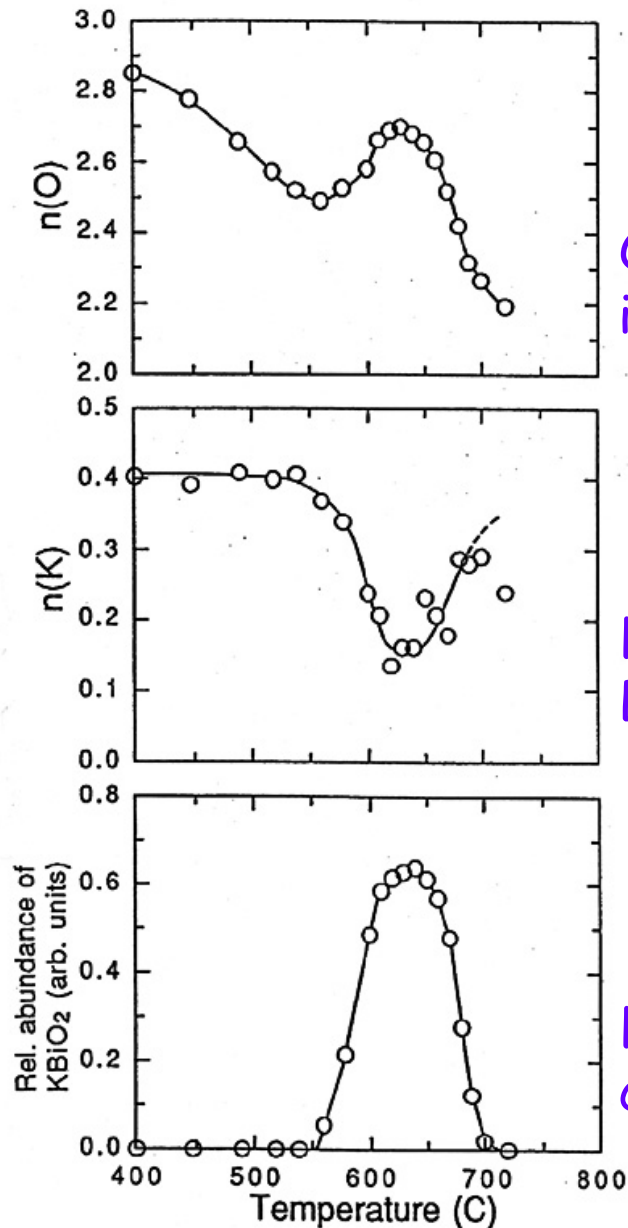
Desired $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$ composition is achieved.

Heating to 400° C in 100% O_2 fills the oxygen vacancies.

Cooling in Ar gives a single phase, but with complex structure due to ordered oxygen vacancies.

Heating in 1% O_2 or Ar. KBiO_2 impurity phase forms, but, desired K solubility is achieved above 700° C.

Synthesis Chemistry of $\text{Ba}_{1-x}\text{K}_x\text{BiO}_{3-\delta}$



Oxygen content
in $\text{Ba}_{1-x}\text{K}_x\text{BiO}_{3-\delta}$

K content in
 $\text{Ba}_{1-x}\text{K}_x\text{BiO}_{3-\delta}$

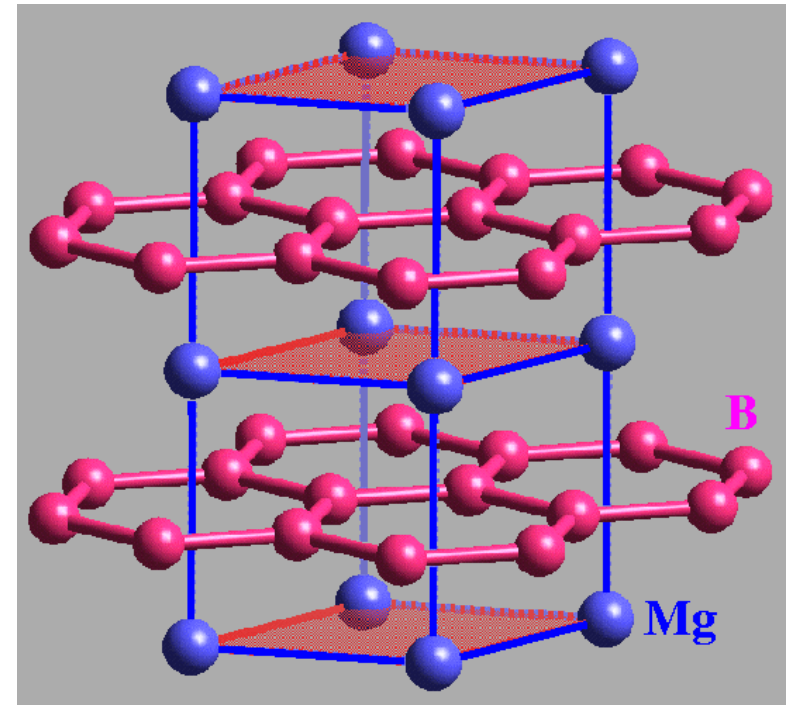
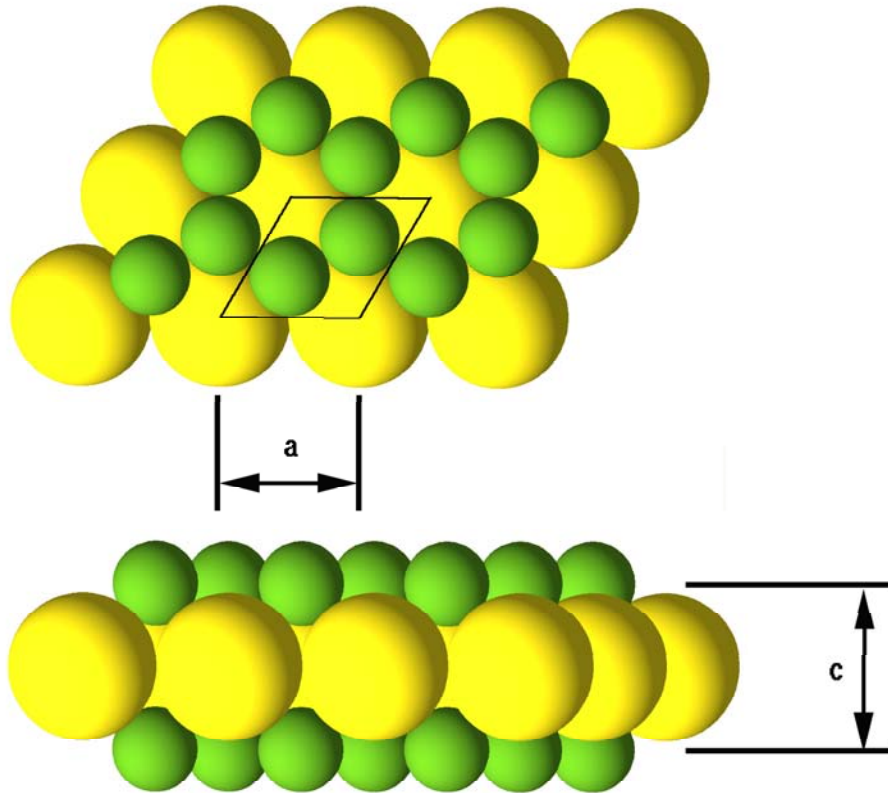
KBiO_2 impurity
content

Conclusion:
K solubility is
controlled by
the Bi oxidation
state.

Pei et al., J. Solid State Chem. 95, 29 (1991)

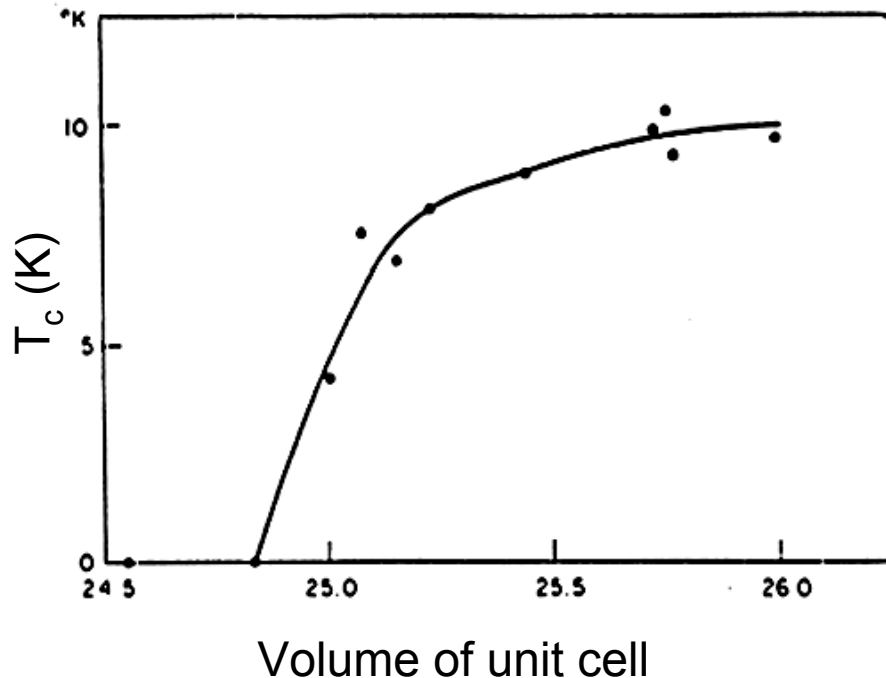
NICEST, 12 March 2003

MgB_2 : $T_c = 39 \text{ K}$



Two equivalent views of the structure

Previous work on hexagonal diborides by the group of B. Matthias



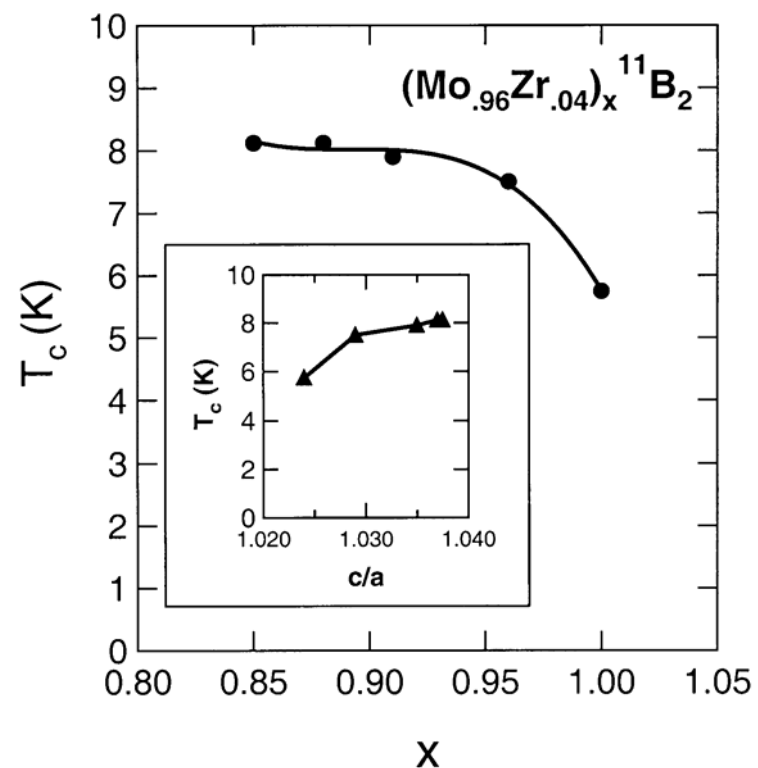
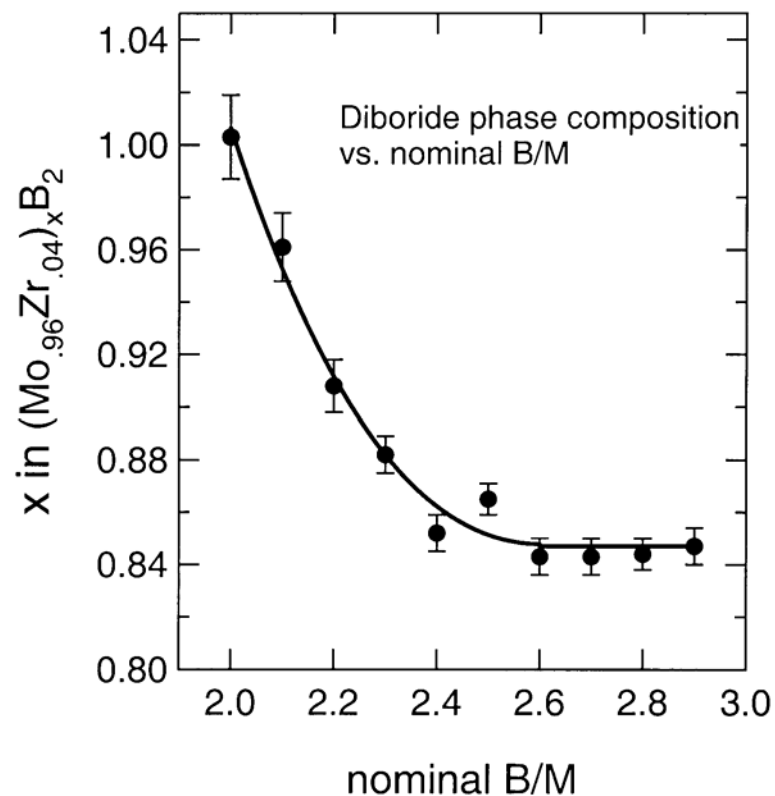
Increase in T_c with
increasing amounts of
Zr substituted in MoB_2

$T_c \approx 11$ K for
 $\text{Mo}_{0.87}\text{Zr}_{0.13}\text{B}_{2+x}$

Note that they claimed the
materials were B rich.

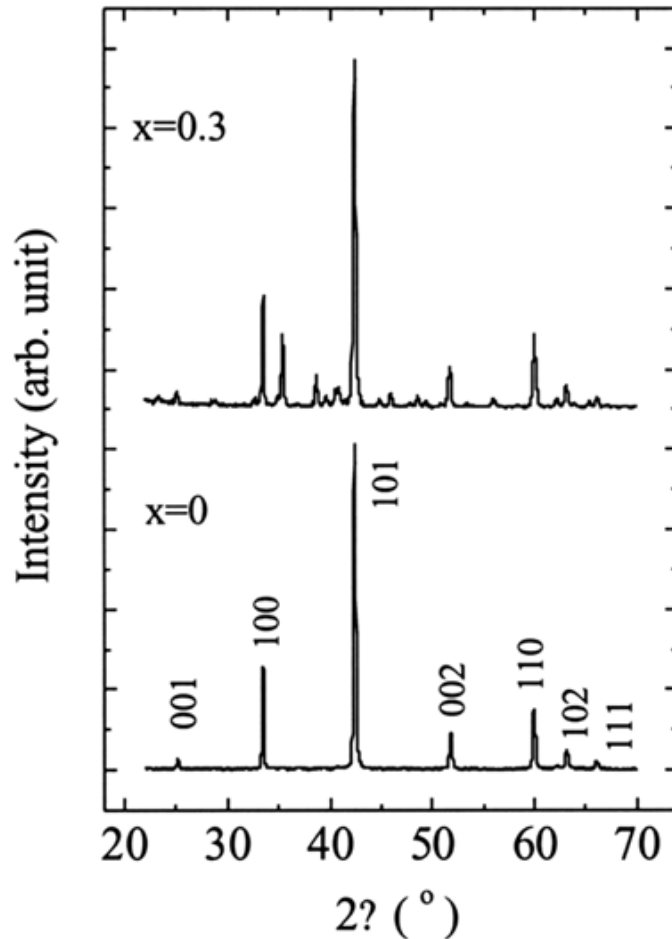
A. S. Cooper, E. Corzenwit, L. D. Longinotti,
B. T. Matthias, W. H. Zachariasen, Proc. Nat'l.
Acad. Sci., 67, 313 (1970)

Properties of $(\text{Mo}_{0.96}\text{Zr}_{0.04})_x\text{B}_2$ versus x



L. E. Muzzy, M. Avdeev, G. Lawes, M.K. Haas, H.W. Zandbergen, A.P. Ramirez, J.D. Jorgensen, and R.J. Cava, *Physica C* **382**, 153-165 (2002)

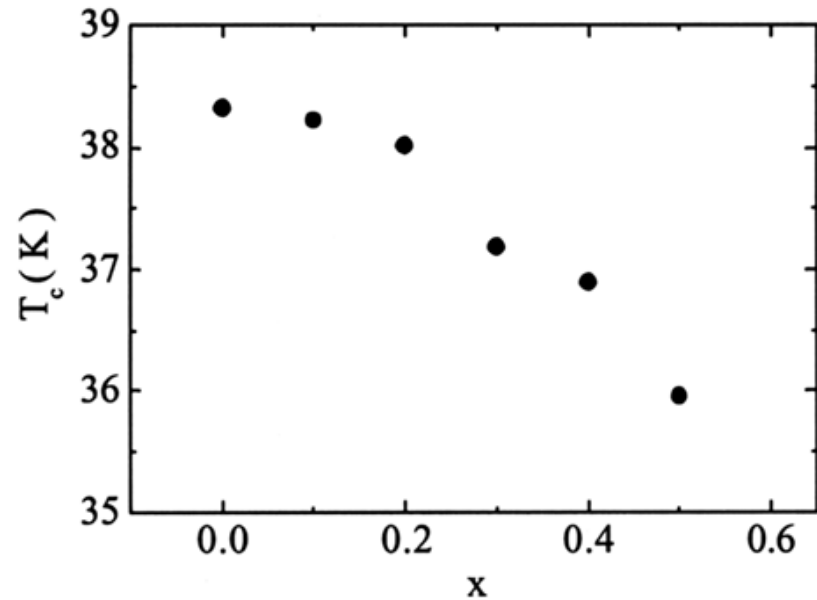
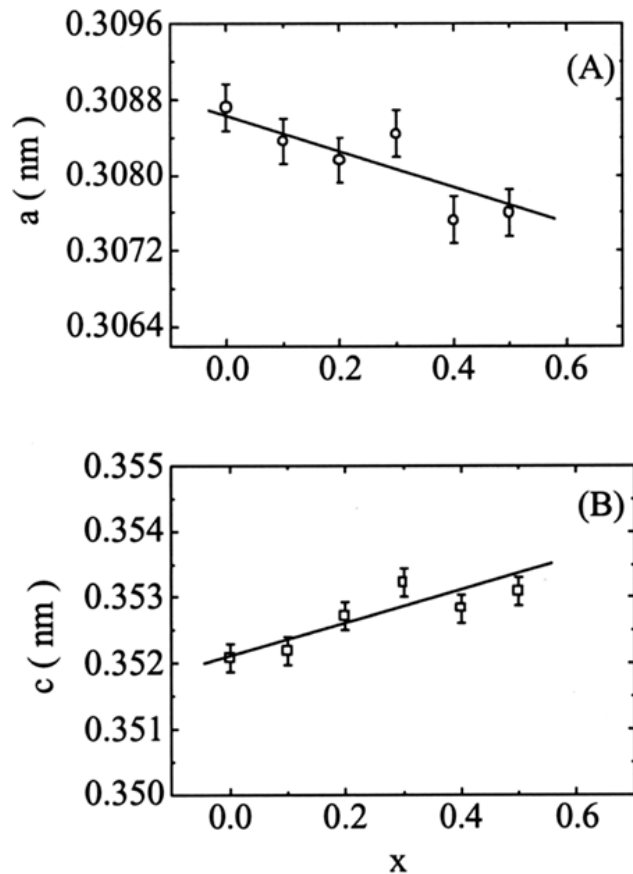
Can the stoichiometry of MgB_2 be varied?
(i.e., can we make $\text{Mg}_{1-x}\text{B}_2$?)



When the starting composition is made Mg-deficient, MgB_4 appears as an impurity phase. This result indicates that MgB_2 is a stoichiometric compound under these synthesis conditions (950°C).

Y. G. Zhao et al., *Physica C* 361, 91 (2001)

However....



Y. G. Zhao et al., Physica C 361, 91 (2001)

Lattice constants change slightly and T_c decreases slightly. There is some kind of effect that is not yet understood. **Gibb's phase rule appears to be violated.**

MgB₂ Synthesis in an Overpressure of Argon Gas



Synthesis furnace:
850° C, 50 atm. Ar

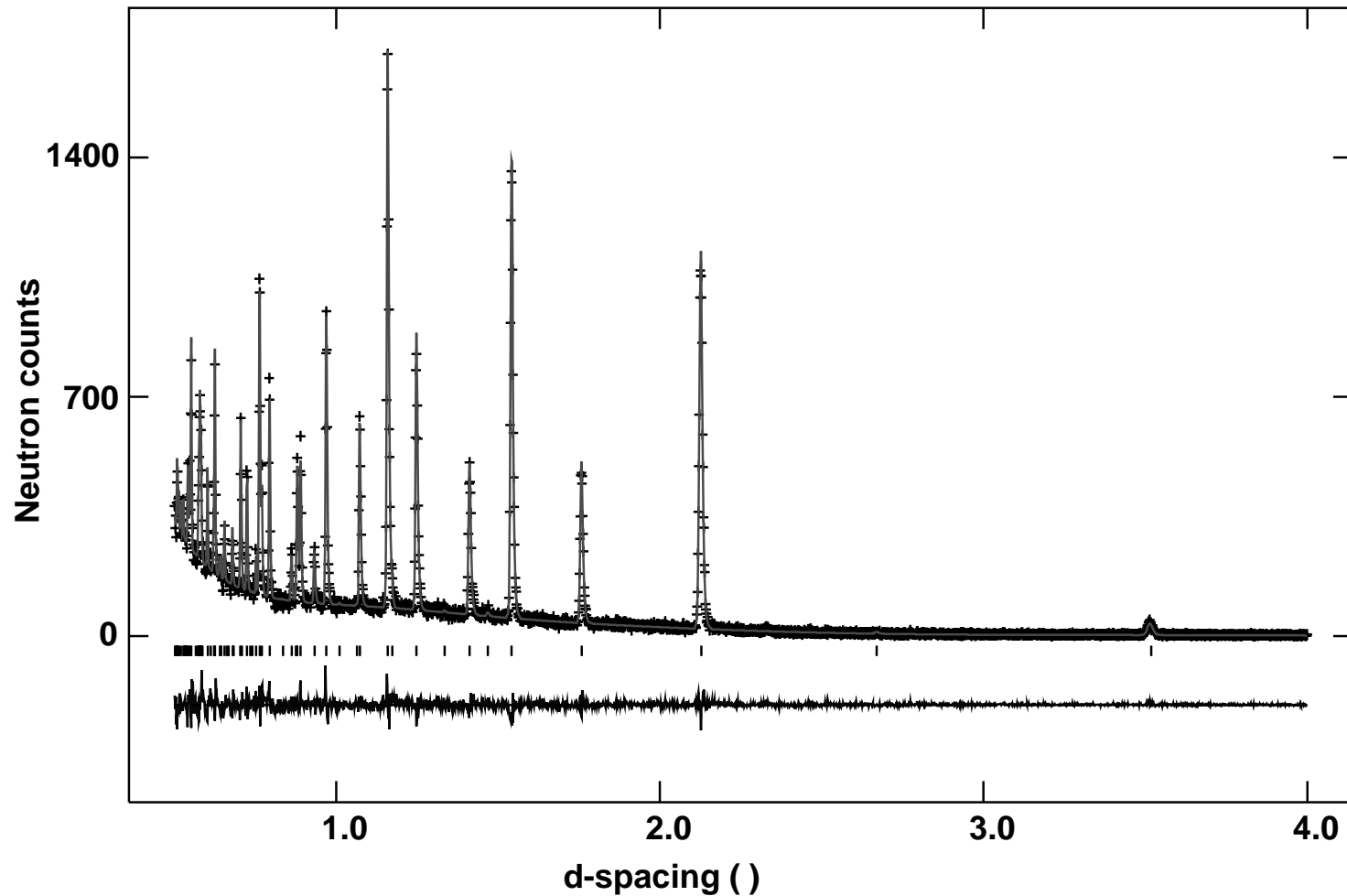


BN crucible



Typical MgB₂ samples

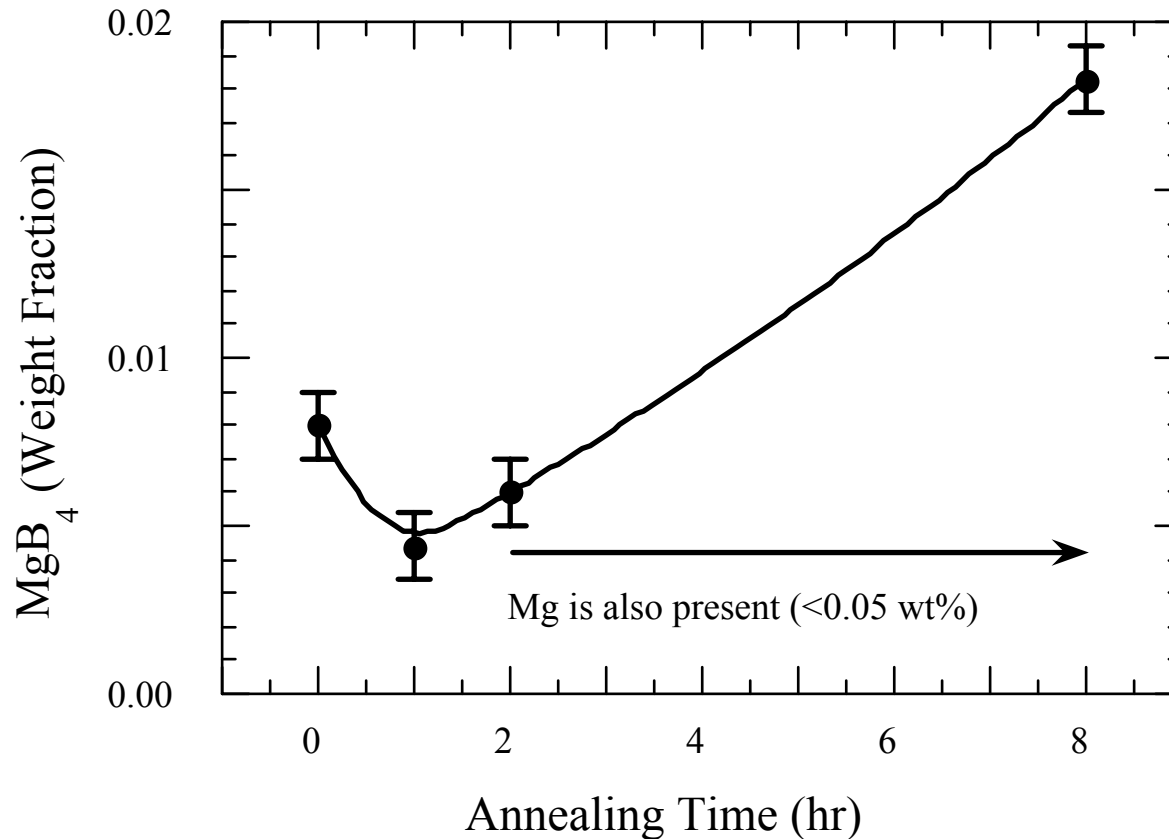
Neutron Powder Diffraction Data from MgB_2



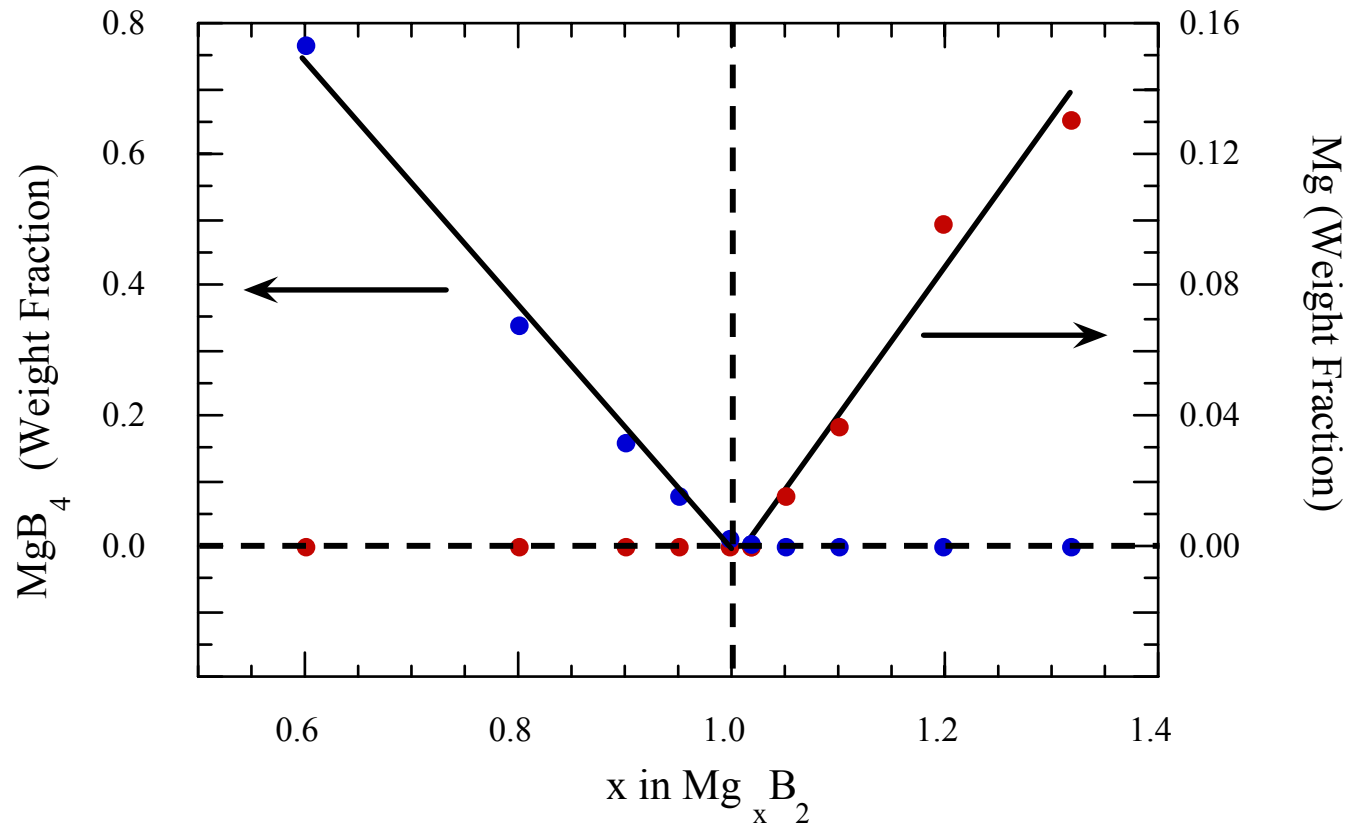
J. D. Jorgensen, D. G. Hinks, S. Short,
Phys. Rev. B 63, 224522 (2001)

NICEST, 12 March 2003

Confirmation that the synthesis technique achieves near-equilibrium conditions



Observation of the expected impurity phases in the expected amounts shows that MgB_2 is a line compound

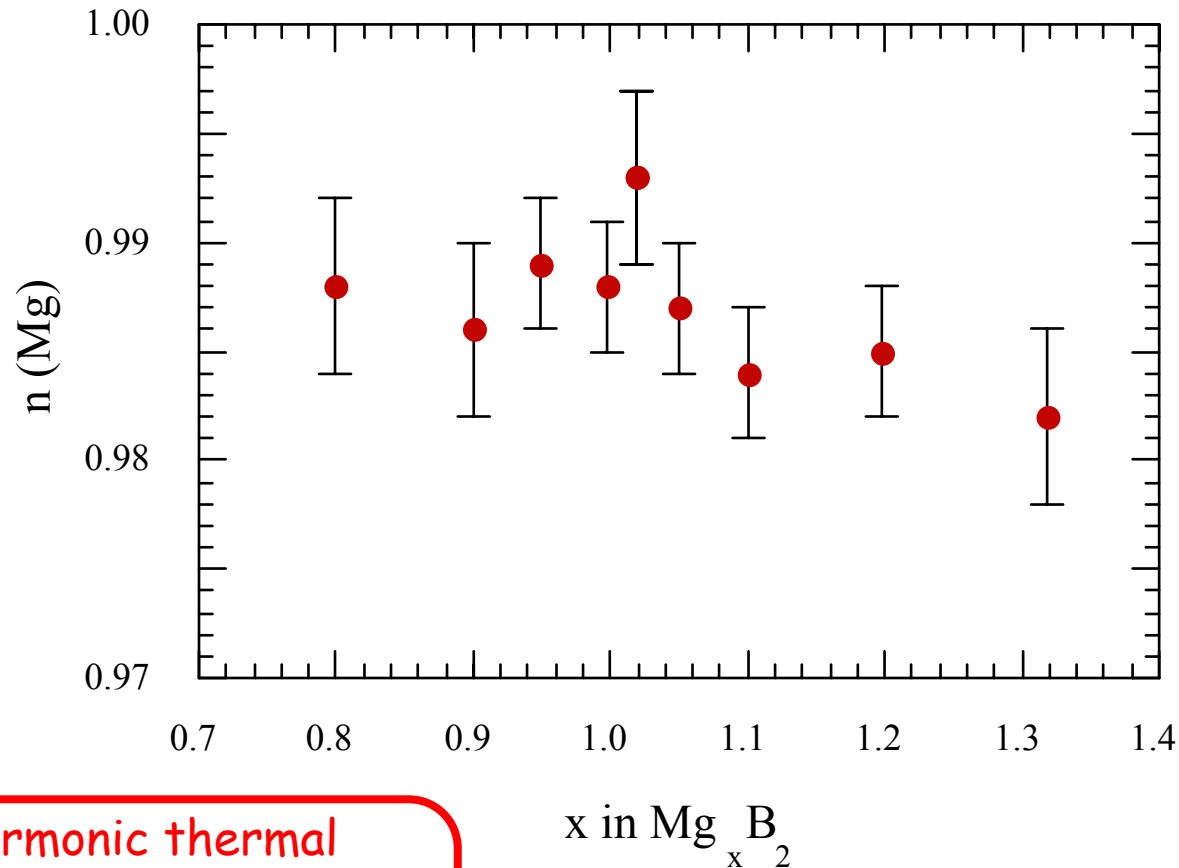


Note that the composition appears to be slightly Mg rich.

D. G. Hinks et al., *Physica C* **382**, 166-176 (2002)

NICEST, 12 March 2003

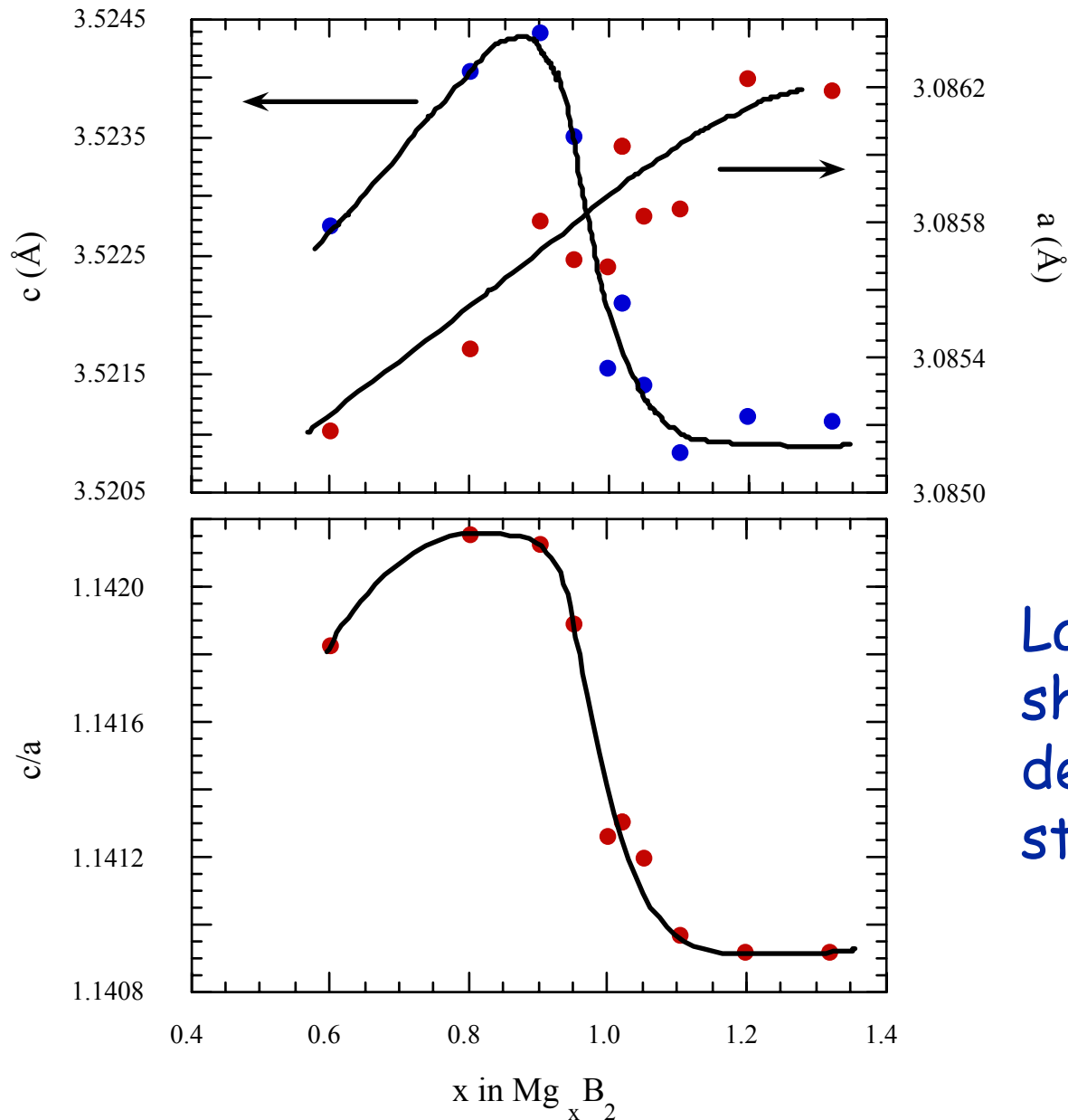
Refinement of the Mg-site occupancy suggests a small constant Mg deficiency; i.e., Mg vacancies



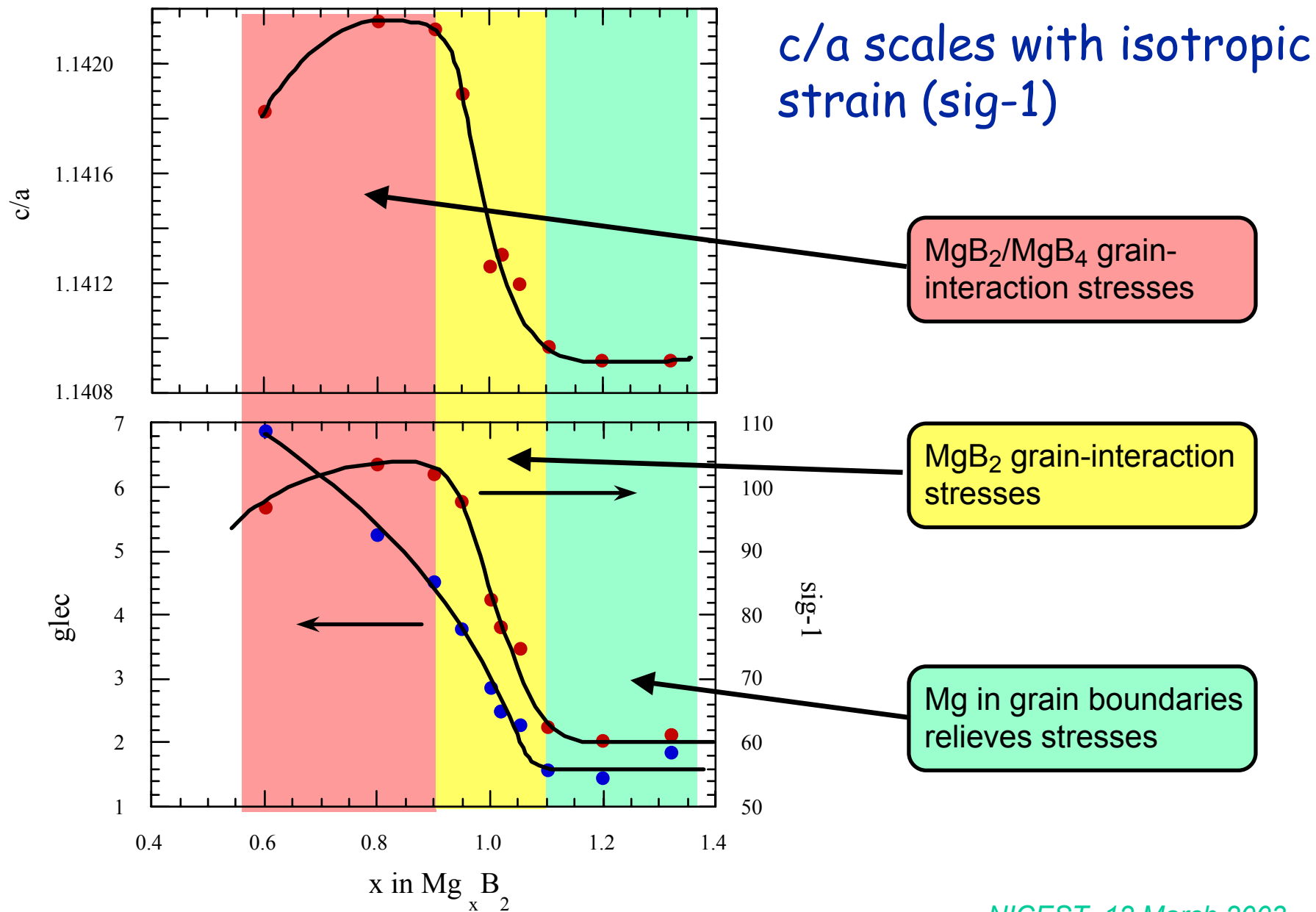
Note: Anharmonic thermal motion or chemical substitution can mimic Mg vacancies in the refinement.

D. G. Hinks et al., Physica C 382, 166-176 (2002)

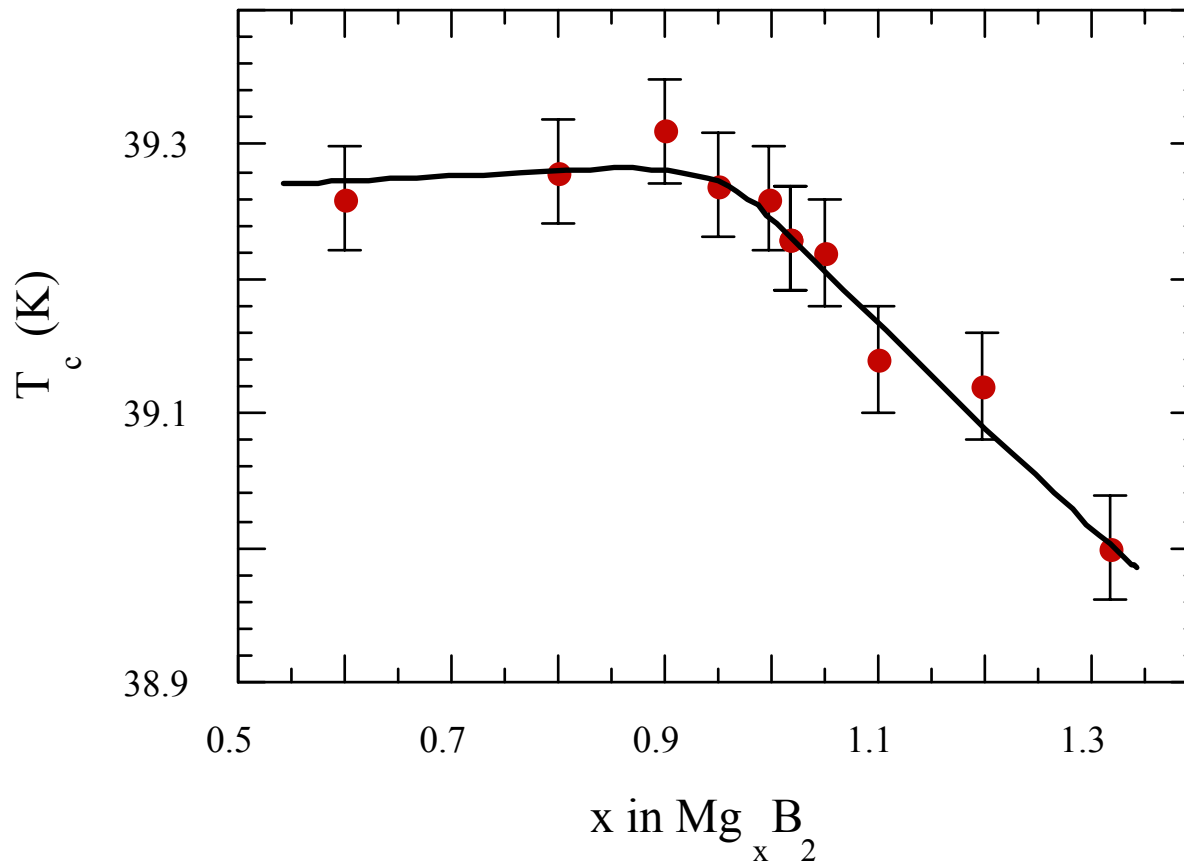
NICEST, 12 March 2003



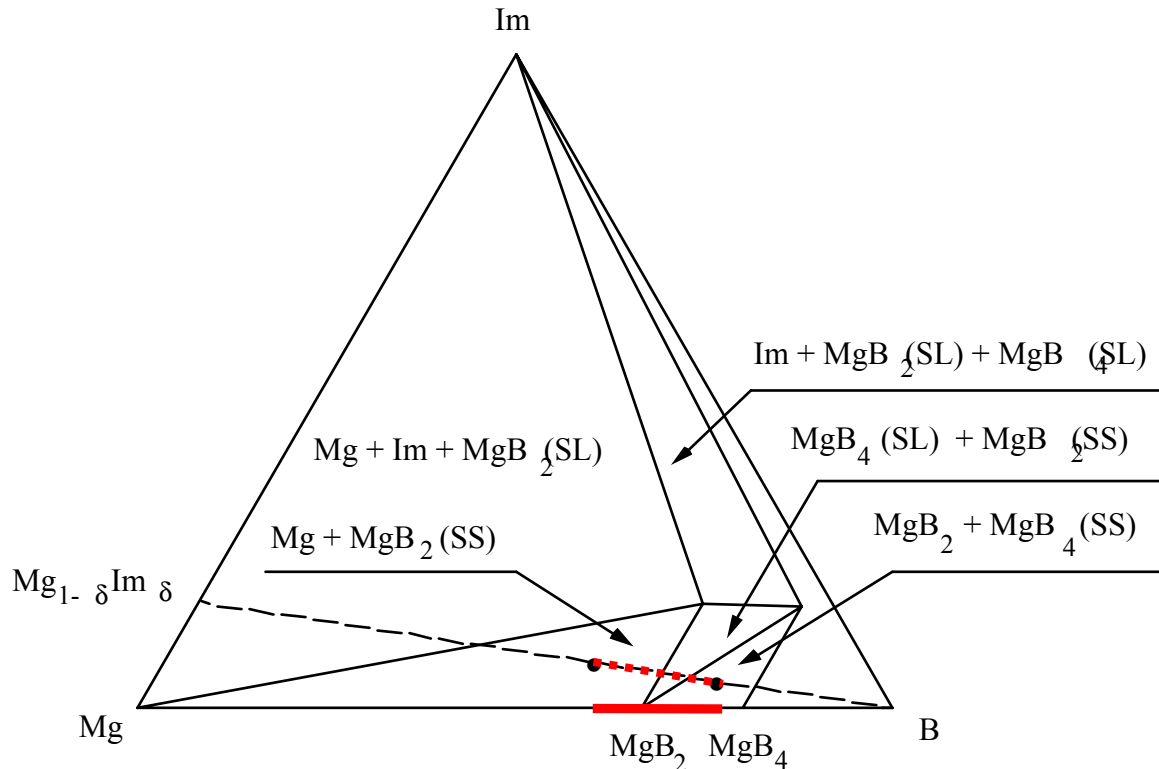
Lattice constants
show a confusing
dependence on
starting composition



T_c decreases slightly with excess Mg. This can be explained by accidental impurity doping.



A phase diagram consistent with the observations



This phase diagram explains:

- The decrease of T_c in the Mg-rich region
- The maximum T_c at a slightly Mg-deficient composition rather than an MgB_2

Advice for Rietveld Refiners

- If you really want to get the best results, try to go beyond using Rietveld refinement as a "black box." Learn how the instrument calibration is done and confirm that it is done correctly. Understand what is in the parameter file.
- Check results against other things known about the material. Make full use of other information, including chemical constraints.
- Look carefully at the raw data and Rietveld plot.
- Ask whether your result makes chemical sense (bond lengths, BVSs, etc.).
- Ask whether the error bars obey the expected statistical rules.